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THE ACTION OF CHLORINE UPON UREA, WHEREBY A DICHLORUREA IS PRODUCED.[1]

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Although a few of the more familiar substances containing halogen attached to nitrogen, as, for example, nitrogen chloride, have been known for a long period, it is only within the last 10 years that such compounds have been systematically studied. They form, however, a group of extraordinary interest and play an all-important part in many complex reactions; to illustrate this it is only necessary to refer to the substitution of halogen in anilides and to the well-known method for obtaining amines from amides. I have shown in a series of investigations that hydrogen attached to nitrogen in compounds of the most varied characters may be replaced with ease by chlorine or bromine if suitable conditions are observed, and it may be said, speaking generally, that this can always be done, although the nitrogen halogen derivatives produced may react or undergo isomeric change so readily that they can only with difficulty be isolated.

[1] Paper read before the Royal Society on June 25th, 1908. Communicated by the author for publication.

All compounds in which halogen is directly attached to trivalent nitrogen can take part in certain well-defined reactions characteristic of the linkage. One of the most striking of these group reactions is that with hydriodic acid, whereby at the ordinary temperature the halogen is replaced by hydrogen, and iodine is liberated quantitatively. This reaction, which may be expressed by the general equation

$$:NX + 2HI = :NH + HX + I_2,$$

affords an easy method of analyzing these compounds.

Such a nitrogen halogen derivative is formed as an intermediate product in a reaction with urea, the course of which has never hitherto been explained although it has received an unusual amount of attention as it furnishes a ready method of estimating the quantity of the urea present in a liquid.

When urea is added to a solution of an alkaline hypochlorite or hypobromite it is at once decomposed, nitrogen and carbon dioxide being set free; if an excess of alkali is used the carbon dioxide is fixed, and the nitrogen, which alone escapes, should thus afford a measure of the amount of urea. The reaction is generally represented by the equation

$$CO(NH_2)_2 + 3NaOBr = CO_2 + N_2 + 3NaBr + 2H_2O,$$

which throws no light upon its nature; indeed it obscures it, as it makes it appear to be a case of oxidation. It does not even express quantitatively what takes place, for all chemists who have investigated the decomposition have noted that the amount of nitrogen liberated is invariably less than that contained in the urea used. When the operations are carried out under specified conditions this loss of nitrogen, which may amount to as much as half of the total, is very constant and so can be allowed for by adding a definite fraction of the whole to the gas actually measured. The method can thus be made to give results sufficiently accurate for clinical purposes and since it is easy to carry out it has received very general application. It is not known what becomes of the nitrogen which does not appear as gas, for all the sug-

gestions that have been made hitherto wholly fail to account for more than a small fraction of the quantity that disappears.

If the urea, instead of being added to an alkaline solution of a hypochlorite, is added to one acidified by acetic acid, that is, to a solution of hypochlorous acid, no gas is evolved, nor is any gas liberated if chlorine itself is passed into a solution of urea in acetic acid. Action takes place, however, in each case and a nitrogen chloride is produced; for although the hypochlorous acid or chlorine disappears, the resulting solution liberates iodine in large quantity from hydriodic acid.

The isolation from such a solution of the substance produced is not practicable, since the method of extraction by chloroform which often serves for the separation of substituted nitrogen chlorides cannot be used, as the chlorurea formed is easily soluble in water but almost insoluble in chloroform. It is, however, less soluble in water than urea itself and crystallizes out in a pure condition when chlorine in excess is passed rapidly through a cooled and sufficiently strong aqueous solution of urea. The action which takes place is represented by the equation

$$CO\begin{matrix}NH_2\\NH_2\end{matrix} + 2Cl_2 = CO\begin{matrix}NHCl\\NHCl\end{matrix} + 2HCl,$$

two only of the four hydrogen atoms of the urea being replaced by chlorine.

This dichlor derivative appears to be the only stable nitrogen chloride which urea is capable of forming. The crystals which separate from the solution of urea have this composition from the first and chlorine seems to have no further substituting action upon them.

Considering its mode of formation, as well as the structure of urea itself, dichlorurea has most probably the constitution represented by the formula $O:C\begin{matrix}N<\begin{matrix}Cl\\H\end{matrix}\\N<\begin{matrix}H,\\Cl\end{matrix}\end{matrix}$, which explains its formation and such of its reactions as have so far been studied.

If this constitution be granted it seems probable that the reaction between urea and chlorine takes place in two stages and that the amino groups are substituted successively, but the monochlor derivative does not crystallize out, possibly because its solubility is not far removed from that of urea itself. Either of two causes may prevent the formation of a tri- or tetrachlor derivative; the hydrochloric acid which is formed in the reaction may prevent the addition of chlorine to the nitrogen which must precede further substitution, or the more highly substituted urea may be hydrolyzed so easily that it breaks up as soon as it is formed. Dichlorurea is so much more easily hydrolyzed than urea itself that the latter is the more probable cause.

Although two molecules of hydrogen chloride are formed when chlorine acts on urea, very little heat is developed. Dichlorurea must, therefore, be an endothermic compound and might be expected to be highly explosive. When heated, however, it does not itself explode but decomposes with liberation of nitrogen chloride which, if heated to a few degrees above the temperature at which it is set free, may detonate with great violence.

Dichlorurea gives all the characteristic reactions of a typical nitrogen chloride; for instance, it liberates iodine from hydriodic acid and chlorine from hydrochloric acid, and reacts with alcohol, forming ethyl hypochlorite, urea being in each case re-formed.

It is distinguished from most other substituted nitrogen chlorides by the readiness with which it is hydrolyzed in presence of water, with formation of nitrogen chloride, carbon dioxide, a little nitrogen, and ammonium chloride. If the compound is dissolved in water or kept in a moist atmosphere, this hydrolysis takes place slowly at the ordinary temperature and becomes very rapid at about 30° C.

It is probable that in this reaction a monosubstituted ammonia is first produced, thus:

$$CO\begin{matrix}NHCl\\NHCl\end{matrix} + 2H_2O = CO\begin{matrix}OH\\OH\end{matrix} + 2NH_4Cl;$$

but if it is, it apparently can exist only momentarily, as nitrogen chloride is at once liberated. The formation of the end products of the reaction can be explained by assuming that this monochlorammonia at once breaks up into ammonia and nitrogen chloride,

$$3NH_2Cl = 2NH_3 + NCl_3,$$

which then react to some extent, forming nitrogen and hydrogen chloride, the latter at once combining with the free ammonia and allowing the remaining nitrogen chloride to escape, as this does not react with ammonium chloride. Both acids and alkalis accelerate the rate of hydrolysis and also alter the nature of the end products by hindering or furthering the secondary reaction between the ammonia and the nitrogen chloride.

In presence of dilute acids the ammonia is at once fixed and the reaction between it and the nitrogen chloride, with its accompanying liberation of nitrogen, is prevented, all the chlorine contained in the dichlorurea being therefore liberated as nitrogen chloride. In presence of alkalies, on the other hand, the reaction between the ammonia and the nitrogen chloride goes on to completion, since the hydrochloric acid formed in it is at once fixed; no nitrogen chloride, therefore, is set free, since twice as much ammonia is formed as is required to decompose it.

The reaction between dichlorurea and a solution of caustic potash is instantaneous: nitrogen is liberated with violent effervescence, the excess of ammonia and the alkaline carbonate formed remaining dissolved in the liquid. The action, which is quantitative, is expressed by the equation

$$3CO\begin{matrix}NHCl\\NHCl\end{matrix} + 12KOH = 3K_2CO_3 + 2NH_3 + 6KCl + 2N_2 + 6H_2O.$$

The behavior of dichlorurea with alkalis affords an explanation of the course of the reaction which occurs when urea is decomposed by an excess of either alkaline hypochlorite or hypobromite. The urea is, without doubt, converted into

dichlor- or dibromurea,[1] which is at once hydrolyzed in the manner above described. In presence of the excess of hypochlorite or hypobromite, the monosubstituted ammonia formed in the hydrolysis may be further substituted to a greater or less extent, nitrogen being evolved quantitatively only when this takes place under such conditions that the amount of hydrogen attached to nitrogen in the reacting system is always sufficient to react completely with the chlorine attached to nitrogen.

Preparation of Dichlorurea.—The preparation of dichlorurea should be carried out at a low temperature and as rapidly as possible, since, in presence of the hydrochloric acid formed at the same time, hydrolysis so readily occurs and so much nitrogen chloride is produced that if it is carried out at the ordinary temperature, or its duration is unnecessarily prolonged, a poor yield is obtained. It is best, therefore, to work with small quantities, to cool thoroughly, and to pass the chlorine as rapidly as possible. The following procedure gives a good result: Dissolve 20 grams of urea in 40 cc. of water and cool to about —10° C. in a mixture of alcohol and crushed ice.[2] Pass in as rapidly as practicable a stream of chlorine made by dropping strong hydrochloric acid upon bleaching powder. So little heat is evolved in the reaction that with proper cooling the temperature never rises above zero, however rapid the stream of chlorine. Nitrogen chloride is produced from the first and can be recognized by its characteristic smell, but it remains in solution, the liquid, owing to its presence, becoming bright yellow in color. After passing the chlorine for a considerable time, white crystals make their appearance, at first usually on the surface of the liquid; these increase in amount till the whole becomes a pulp of thin,

[1] It is possible that in absence of free acid, and in presence of excess of hypochlorite or hypobromite, a tri- or tetrahalogen substitution product may be produced, the formation and decomposition of which can be formulated easily, but this does not affect the essential character of the reaction, which is one of halogen substitution followed by hydrolysis of the substituted urea and interaction between the resulting compounds.

[2] It is not absolutely necessary to use a freezing mixture. The temperature, owing to the solution of the urea, falls at once to below zero, and if the flask in which the operation is carried out is cooled by tap water, a moderate amount of the compound can be obtained, but the yield is much better at a lower temperature.

colorless plates. When these no longer appear to increase in amount, filter off, separating the acid mother liquor as completely as possible; wash once or twice with a little water, and when as much of the latter as possible has been removed wash the crystals several times with dry chloroform. Dichlorurea is not appreciably soluble in cold chloroform and a good deal of adhering moisture is thus got rid of. Press finally between filter paper, spread out in a thin layer on a clock glass, and free from the last traces of water by exposing for about half an hour over phosphoric oxide in a vacuum.

A further crop of crystals can be obtained by again passing chlorine through the cooled mother liquor and this can be repeated as long as any crystals separate. Nothing besides dichlorurea and the products of its hydrolysis are formed in the reaction; if the acid mother liquor is evaporated down, carbon dioxide is given off and nitrogen chloride escapes in quantity; later, as the liquid becomes concentrated, hydrogen chloride is expelled, and finally ammonium chloride is left.

Although the final result of the action which takes place is the substitution of two atoms of hydrogen by two atoms of chlorine, as in other similar cases this is without doubt effected by the addition of four atoms of chlorine to the nitrogen, followed by the elimination of two molecules of hydrogen chloride.

So much of the dichlorurea is hydrolyzed during the process that the yield is not very large: in a well conducted experiment it reaches about 25 per cent of the calculated, the weight of pure dry product obtained amounting as a rule to rather more than half the weight of the urea used. The loss, although largely due to the hydrolysis of the compound, is much increased by the circumstance that dichlorurea is very soluble in water and consequently a considerable amount does not crystallize out from the mother liquor.

Dichlorurea acts with an aqueous solution of hydriodic acid in the way characteristic of nitrogen chlorides; urea is re-formed and iodine quantitatively liberated. It was analyzed by taking advantage of this reaction: a known weight was added to an excess of a solution of potassium iodide made acid

by acetic acid and the iodine liberated estimated by a standard solution of sodium thiosulphate.

0.5112 gram liberated iodine = 158.6 cc. N/10 I.

	Calculated for $CON_2H_2Cl_2$.	Found.
Cl as :NCl	54.96	54.99

Dichlorurea cannot be kept for any length of time without change. When damp it hydrolyzes exactly as when dissolved in water. To obtain it pure, therefore, it must be dried very rapidly over phosphoric oxide in a vacuum. When freed from adhering water only as far as is possible with a pump, it is slowly hydrolyzed by the retained moisture even though placed in a desiccator over strong sulphuric acid, and this often occurs to such an extent that the mass becomes quite yellow from the nitrogen chloride mechanically retained by the crystals. To show the amount of hydrolysis which takes place under these conditions a quantity of the pure substance thus freed from all but adhering water was kept over strong sulphuric acid, and analyzed from time to time, the nitrogen chloride formed being allowed occasionally to escape. In two days the percentage of chlorine as :NCl had fallen to 43.79, and in seven days to 13.33.

Even when dried and kept over phosphoric oxide it slowly decomposes, nitrogen chloride being evolved. A quantity of the pure dry compound thus preserved in a vacuum over phosphoric oxide was analyzed at intervals; after 12 hours the percentage of chlorine as :NCl had fallen to 54.67, after two days to 52.97, and after nine days to 47.87 per cent.

When an aqueous solution is kept at the ordinary temperature the dichlorurea is slowly hydrolyzed; carbon dioxide, a little nitrogen, and nitrogen chloride escape, and ammonium chloride remains in solution. Complete hydrolysis by water requires many days unless the aqueous solution is warmed, when it is much more rapid; at about 20° bubbles of gas are freely evolved and rapid effervescence sets in at about 40°, the nitrogen chloride escaping without explosion.

Dichlorurea prepared as described above is a soft, white, crystalline power with a pearly lustre. Under the microscope

it is seen to consist of thin transparent plates somewhat irregular in shape. It can be recrystallized from water, in which it is easily soluble and from which it separates in similar but larger plates, by cooling an aqueous solution saturated at about 15° C., though there is some loss owing to hydrolysis. Its aqueous solution is at first colorless but becomes yellow as hydrolysis proceeds, owing to the liberation of yellow nitrogen chloride which remains dissolved in the water. It is easily soluble in alcohol and ether, very slightly soluble in chloroform, and soluble in petroleum ether. When its alcoholic solution is heated it reacts in the way characteristic of nitrogen chlorides, urea is re-formed, and ethyl hypochlorite is produced, the latter very easily breaking down into aldehyde and hydrogen chloride.

Its behavior with acids is complicated by the circumstance that it is so readily hydrolyzed; for example, when it is added to strong hydrochloric acid, though chlorine is rapidly given off, the amount of urea re-formed is not very large. When placed in cold strong sulphuric acid it is hydrolyzed and nitrogen chloride is liberated. The latter decomposes into its elements if the liquid be heated, its characteristic smell disappearing and being replaced by that of chlorine.

Dichlorurea is a compound of a marked acid character; it has an acid taste recalling that of hypochlorous acid, and its aqueous solution strongly reddens litmus paper, which becomes bleached only after the lapse of some minutes. It acts very corrosively upon the skin, staining it yellow and destroying the tissues.

When heated, dichlorurea melts with decomposition at about 83°, nitrogen chloride being liberated. Although the substance itself appears not to explode, if the temperature of the bath in which the melting point is being taken is allowed to rise at all rapidly a few degrees above this point, the nitrogen chloride set free in the tube may explode with considerable violence.

If thrown in quantities of not more than about half a gram at a time into a porcelain dish heated to 100° on a water bath, it can be decomposed without danger. The white

compound fuses and gives off nitrogen chloride as a yellow vapor which escapes quietly unless too large a quantity of material is decomposed at once, when some of the vapor is mechanically retained as bubbles in the semifused residue and thus becomes heated to the temperature at which it explodes. Hydrogen chloride is not set free when dichlorurea is thus decomposed by heat.

When an aqueous solution of the compound is added to a solution of caustic soda vigorous effervescence, due to escape of nitrogen, occurs. The liquid remaining contains ammonia and potassium carbonate, the volume of carbon dioxide liberated when this is treated with an acid being to the volume of nitrogen previously liberated as 3:2. One third of the nitrogen contained in the dichlorurea used is found as ammonia.

The investigation of dichlorurea, which is an extremely reactive body and promises to be of considerable use in organic synthesis, is being continued.

The thanks of the author are due to Dr. Baker for allowing him to use the Christ Church Laboratory, where this work has been carried out.

THE REGULATION OF TEMPERATURE IN THE MEASUREMENT OF OSMOTIC PRESSURE.[1]

By H. N. Morse and W. W. Holland.

The more recent improvements in the manometers and cells which are used in the measurement of osmotic pressure have already been described.[2] The subject of the present paper is the methods which have been adopted for the purpose of securing constant temperatures in the various baths employed in the work.

The regulation of temperature in the measurement of osmotic pressure presents certain unusual difficulties, the grav-

[1] The work upon osmotic pressure which is in progress in this laboratory is aided by grants from the Carnegie Institution. The earlier papers upon the subject will be found in This Journal, **26**, 80; **28**, 1; **29**, 173; **32**, 93; **34**, 1; **36**, 1 and 39; **37**, 324, 425, and 558; **38**, 175; **39**, 667; **40**, 1, 194, 266, 325; and **41**, 1.

[2] This Journal, **40**, 266 and 325.

ity of which appears not to have been fully realized by most of those who have attempted to measure the force. The principal source of these peculiar difficulties lies in the fact that the osmotic cell, filled, as it is, with a considerable volume of a liquid having a large expansion coefficient, and joined to a manometer of small bore, is itself an exceedingly sensitive thermometer. It is clear that *osmotic effects* cannot be distinguished from the "*thermometer effects*" resulting from fluctuations of temperature. It is obvious, moreover, that *thermometer effects* in the cell can be *wholly* eliminated in one way only, and that is by maintaining in the bath a temperature so nearly constant that its fluctuations cease to produce a sensible effect upon the volume of the liquid enclosed in the cell. The ideal solution of this difficult problem would be a regulation so exact that not even the form of the mercury meniscus in the manometer could be sensibly affected by variations in the volume of the enclosed solution. This is the end to be striven for, although the task imposed is perhaps an impossible one. It must not be imagined that so high a degree of temperature regulation is unnecessary, and therefore absurd. On the contrary, even the variation in the form of the meniscus becomes a matter of importance whenever it is attempted to measure the osmotic pressure of concentrated solutions.

Since any pressure in the cell which exceeds the osmotic pressure of the solution necessarily forces a portion of the solvent out of the cell, while any under-pressure causes some of it to enter, it might be inferred that decided *thermometer effects* would become manifest only when the enclosed solution is subjected to rapid and large changes of temperature. But this is not the case. When the maximum osmotic pressure of a solution has once been developed in the cell, any subsequent readjustment between it and a thermometer effect due to an expansion or contraction of the solution is very slow; and especially so in cells in which considerable membrane has accumulated through long use, and in those also in which the membrane is of small area. In other words, when the osmotic pressure is nearly at a maximum, the trans-

ference of solvent in either direction through the membrane becomes very tardy. In this way is to be explained the fact, frequently observed, that the full recovery from a thermometer effect often requires several hours—nearly as much time, in fact, as did the development of maximum pressure after closing the cell. To give a concrete illustration of what is always observed when a change of temperature occurs in the bath, we will suppose that—after the maximum pressure has been developed in a cell and the height of the mercury in the manometer has remained practically constant for a long time, *e. g.*, an entire day— the temperature of the water in the bath undergoes a slight alteration. If the change is a rise in temperature, it is quickly followed by a rise of the mercury in the manometer, while a fall in temperature is as promptly followed by a descent of the mercury column. Moreover, to one who has not been duly impressed with the sensitiveness of the osmotic cell as a thermometer, the magnitude of the rise or fall of the mercury in the manometer—more precisely, the change in pressure—will seem out of all proportion to that of the change in the temperature of the solution. Now, although the solution may quickly regain its original temperature, the restoration of the original pressure will not be complete for several hours. The full recovery from the "*thermometer effect*" will, in fact, as previously stated, consume nearly as much time as did the development of the original maximum pressure. But the recovery may not be complete; for other changes of temperature may intervene before the requisite time for complete recovery has elapsed, introducing new complications, the nature and effect of which are too obvious to require explanation. An examination of our records will show that the pressure of the solution very rarely remains perfectly constant throughout an experiment. In nearly every case, slight fluctuations have been observed, even when the recorded temperatures of the bath have shown no variation. We have made a long and careful study of these ever-recurring fluctuations of pressure while the cells are in the bath, with a view to determining their cause or causes. A sufficient explanation of them

ol. 41
1909

is to be found in the possible slight variations in the volume of the solution in the cell, combined, of course, with the well-known very slow passage of solvent through the membrane when pressure is nearly at a maximum; but there is another possible cause, namely, the breaking and mending of the membrane. The latter process, even if it exists, cannot be directly studied, hence we were obliged to content ourselves with ascertaining whether the fluctuations in question are *always accompanied by*, or *follow*, changes in the temperature of the bath. In every instance which has been brought under systematic observation, the variations in pressure—amounting perhaps only to changes in the form of the meniscus—have been identified as *thermometer effects*.

The recorded observations of pressures and temperatures in a given experiment are sometimes seemingly quite contradictory, as when the temperatures at the time of successive readings are found to be identical, while the pressures are different, or when the higher pressure is found to correspond to the lower of two temperatures. A little reflection, however, will show that both of these seemingly inconsistent situations are not only the possible, but frequently even the probable, results of *thermometer effects*.

Enough has been said to emphasize the necessity for the most careful regulation of temperature in the baths in which the cells are placed for the measurement of pressure. The need of such regulation does not, however, begin with the placing of the closed cells in the bath. It is a peculiarity of solutions that, when they are surrounded by a rigid semi-permeable membrane, they are able—through a process of concentration or dilution—to accommodate their volume to any space which may be offered. This fact makes it imperatively necessary that the solutions, at the time of filling and closing the cells, shall have exactly the temperature at which the osmotic pressure is to be measured. Otherwise, the solutions are, to an unknown extent, more or less concentrated than was intended. It is to be remembered here that *concentration* means the numerical ratio of the molecules of the dissolved substance to those of the solvent, and not

the number of the former which is distributed through a unit of space. Now, suppose that a cell is filled with a solution having a lower temperature than that at which it is desired to measure its osmotic pressure and that the cell is then closed and placed in a bath of the required (higher) temperature. The consequence is obvious. The capacity of the cell—that is, the volume which the solution may eventually have—is practically fixed at the time of closing, because the expansion coefficient of the material of the cell walls is small, and the initial mechanical pressure which is brought upon the solution is—or should be—nearly equal to the osmotic pressure, so that the capacity of the cell can be but slightly increased by any subsequent contraction in the volume of the gas in the manometer. The first observed effect of the rising temperature and nearly fixed volume of the solution is a pressure considerably in excess of the true osmotic pressure. This afterwards declines slowly, and finally becomes constant, except as the equilibrium is subsequently disturbed by *thermometer effects*. But the final pressure is still in excess of the true osmotic pressure of the original solution, showing that the solution in the cell has become more concentrated than it was at the time of closing. In other words, the nearly fixed volume of the solution has been maintained, in spite of *rising* temperature, by the expulsion of a portion of the solvent. Suppose, on the other hand, that the solution, at the time of filling and closing the cell, has a higher temperature than that of the bath in which its pressure is to be measured. The fixed volume will then be maintained, in spite of *falling* temperature, by the acquisition of solvent from the outside, *i. e.*, by dilution. The pressure will rise and finally become constant, but it will always be less than the true osmotic pressure of the original solution. The concentration and dilution which take place when cells are filled with solutions having temperatures different from those of the baths are permanent. In this respect, they differ from the changes in concentration which attend *thermometer* effects. The latter are of a temporary character.

Our first cells were set up, without any external protec-

tion, in a room which was subject to the usual variations of temperature. Some measures were taken, however, to moderate the extremes and to avoid very rapid changes of temperature. We were then under the impression that the passage of the solvent through the membrane is much more expeditious than it was afterwards found to be; and that, if the changes of temperature were moderately slow, the solutions would acquire or discharge the solvent with such facility that the observed changes of pressure could be interpreted as truly osmotic in character and due solely to changes in the concentration of the solutions in the cells. We were quickly undeceived. The fluctuations of pressure were far greater than could possibly be ascribed to changes in concentration. It then became clear that we had to deal with the osmotic cell as a *thermometer*, and that, in order to measure osmotic pressure with any degree of precision, the thermometric manifestations of the cell must be suppressed by the maintenance of nearly constant temperature in the bath. As a first step in this direction, the cells were placed in a wooden box with double walls. The spaces between the walls were filled with hair, and the box was both lined and covered with thick hair-felt. It was with this arrangement that the first series[1] of measurements of the pressure of cane sugar solutions was carried out. The fluctuations of temperature were much smaller and slower than before and the thermometer effects were correspondingly less pronounced. They were, nevertheless, still intolerably large. The greatest change in the temperature of a solution while in the box was 4°.48; the smallest was 0°.75; while the mean variation for the whole series of 24 determinations was 2°.03. It should be stated, however, that some of the largest variations were due, in part, to the fact that at that time insufficient attention was given to the temperature of the solutions at the time of filling and closing the cells.

The next effort[2] to secure uniformity of temperature was of a much more elaborate character. A copper-lined rectan-

[1] THIS JOURNAL, **34**, 1.
[2] *Ibid.*, **38**, 1.

gular tank, holding about 300 liters, was constructed and symmetrically fixed in a wooden box of larger dimensions. The considerable spaces between the two were filled with hair, and a superstructure of equal width and depth, but only three-fourths as long, was built over the top of the bath. The front consisted of a plate-glass hinged window, while the top (also hinged) and the remaining sides were double walled and filled with hair. To further protect the enclosed air space above the water against external conditions, the glass front was completely covered with a thick hair pad. This was divided into narrow strips, so that any part of the interior space could be examined without uncovering any large portion of the front. The remaining fourth of the top of the bath—that portion which was not occupied by the house—was covered with boards, on which rested the machinery employed in driving the pumps. There were two pumps. One of them drew the water—at the rate of 20 liters per minute, if necessary—through a pipe lying on the bottom, and delivered it at the top of the bath. The second pump was employed in circulating the air in the enclosed space through a system of pipes lying in the water below, the purpose being to keep the two, if possible, at the same temperature. The arrangement for stirring the water proved to be entirely satisfactory, and it has never been abandoned or even materially modified. That for maintaining the air in the enclosed space at the temperature of the water was not wholly effective, and though never discarded, in the later work it has been supplemented by other devices which will be described below.

As the laboratory was not heated at night, the bath was enclosed by a structure—3.3 meters long, 2 meters in width, and 2.6 meters in height—which consisted of a wooden framework, covered on both sides with thick muslin. The cloth upon the vertical walls was sized with gelatin, to render it less pervious to air without interfering too greatly with the light, while that upon the roof was both sized and painted. The space within the enclosure was heated at night by an electric stove which was controlled by means of a thermo-

stat. The larger room outside was also heated at night, but with a gas stove which was likewise under the control of an electric thermostat. The purpose of these heating devices, which were described in a former paper,[1] was not to maintain a constant temperature throughout a series of measurements, but merely to mitigate the extremes of temperature in the neighborhood of the bath. It was supposed that, with a bath so well protected by nonconducting materials and with a fairly uniform external temperature, the temperature of the large body of water within the bath would change so slowly that *thermometer effects* would be eliminated.

When the preparations just described were completed, a new series[2] of determinations of the osmotic pressure of cane sugar solutions was undertaken. The efficiency of the provisions which had been made for the maintenance of uniform temperature during the individual determinations may be judged by the following statements. The series in question consisted of 23 measurements of pressure. The greatest variation during any one experiment was 0°.95; the smallest was 0°.00; while the mean variation for the whole series was 0°.32. The improvement on the temperature conditions under which the previous series of measurements had been made was very great and we were at that time convinced[3] that the results were but little influenced by *thermometer effects*. This opinion has since been revised, later and more systematic study of these phenomena having shown that much smaller fluctuations of temperature may sensibly vitiate the results.

While the variation in temperature during the time of any individual measurement was not seemingly large, the temperatures from experiment to experiment ranged from 20°.0 to 24°.5. We had not then, as we now have, the means for regulating bath temperature independently of external conditions, and we were, therefore, obliged to conform quite

[1] THIS JOURNAL, **36**, 13.
[2] *Ibid.*, **36**, 39.
[3] *Ibid.*, **36**, 41.

closely to the room temperatures which prevailed during the daytime.

In another bath of identical construction and similarly protected against external conditions, a series[1] of determinations of the osmotic pressure of glucose solutions was carried out. Twenty-five measurements were made. In one experiment the variation in temperature amounted—through a neglect of one of the usual precautions— to 1°.3. The greatest variation among the remaining 24 experiments was 0°.80; the smallest was 0°.00; and the mean variation for the whole series was 0°.31. The highest average temperature at which any measurement was made was 26°.9, and the lowest was 21°.9.

During the following winter (1907) two series of measurements—one of cane sugar[2] and the other of glucose[3] solutions—were made at temperatures in the vicinity of 0°. To prepare for the work at the lower temperatures, all available space in one of the baths—both in the water and in the air enclosure above—was filled with perforated galvanized iron ice boxes, and provision was made for the automatic discharge of the water which accumulated from the melting of the ice. In other respects the bath was not essentially changed. In the case of the cane sugar series, the highest mean temperature during any one of the 27 experiments was 0°.32, while the lowest was 0°.14. The greatest variation in temperature during any experiment was 0°.24; the least was 0°.00; and the mean variation for the whole series was 0°.10. The regulation of temperature in the glucose series, which followed that of cane sugar, was slightly better. Here, the highest mean temperature during any one of the 20 experiments was 0°.28; and the lowest, 0°.08. The greatest variation in temperature during a single measurement was 0°.23; the smallest, 0°.01; while the mean fluctuation in temperature for the whole series was 0°.08.

After the completion of the measurements of pressure in the vicinity of 0°, the work entered upon a new phase

[1] THIS JOURNAL, **37**, 324.
[2] *Ibid.*, **37**, 425.
[3] *Ibid.*, **37**, 558.

in respect to the regulation of temperature. It was desired to determine the osmotic pressure of cane sugar and glucose solutions at various temperatures between 0° and the ordinary room temperatures. The agent which seemed to lend itself most readily to this purpose was the hydrant water. During a few weeks in the coldest season, its temperature is ordinarily about 4°.0, while in midsummer, it may, for a short time, exceed 25°. It was thought that by appropriately choosing the season various fairly uniform temperatures could be maintained in the bath for considerable periods by means of running water, or, at least, that the fluctuations would not necessarily exceed those which had been experienced while measuring pressure at room temperature. Accordingly, one of the baths was provided with a system of pipes through which the hydrant water could be made to circulate at any desired rate. A series of connected vertical brass pipes, having a length, individually, of nearly a meter, an external diameter of 20 mm., and an internal diameter of 16 mm., was arranged around the four interior walls of the bath. The distance between the pipes was 50 mm. Each pipe extended from a point near the top of the air space to a depth of 36 cm. under the water below, except for a short distance in front of the window, where the pipes were shorter and did not enter the water. A second series of connected horizontal pipes —as long as the bath, and likewise 50 mm. apart—was suspended close to the top of the air space. The section of pipes in front of the window was removable, being connected, by means of flexible hose couplings, on the one hand to the remainder of the vertical system, and on the other to the horizontal system above. Means were also provided for moving, without opening the bath, the section of pipes in front of the window whenever a pipe was found to obstruct the view of a manometer. The circulating water passed continuously, first through the system of vertical pipes, and then through that of the horizontal pipes in the upper part of the air space. The superficial area of all the pipes above the water was equal to that of all the walls of the air space, including that of the top; and its ratio to the surface of the submerged pipes was

about as 2 to 1. The water employed in regulating the temperature of the bath was brought in a large pipe directly from the basement, and there were no intervening outlets.

When the arrangement described above had been completed, it was attempted to measure the osmotic pressure of cane sugar solutions in the vicinity of 5°.0;[1] but, as the series could not be finished before the beginning of April, it was necessary at times, especially in the latter part of the work, to cool the circulating water with ice. The efficiency of the device in regulating the temperature of the bath can be best judged by the following table in which the mean bath temperature and the extreme variations in temperature are given for each of the 20 experiments.

Table I.

Mean bath temperatures.	Extreme variation.	Mean bath temperatures.	Extreme variation.
4°.84	0°.80	5°.03	0°.50
4°.93	0°.80	6°.05	0°.45
4°.58	0°.60	4°.35	0°.30
6°.05	0°.65	4°.55	0°.35
4°.50	0°.15	4°.48	0°.75
4°.50	0°.15	4°.33	0°.15
4°.48	0°.90	4°.33	0°.10
4°.51	0°.70	5°.23	0°.50
4°.34	0°.50	4°.60	0°.70
5°.23	0°.50	4°.32	0°.35

It appears from the table that the maximum change in the temperature of the bath during any one experiment was 0°.9; the minimum, 0°.1; while the average variation for the whole series was 0°.5. The control of temperature by means of running water had proved, in the first attempt, to be somewhat less satisfactory than that which had been secured at room temperature by the means previously described; and there could be no doubt that the results, like those of the earlier series, were vitiated to some extent by thermometer effects.

The idea of securing uniform temperatures by means of running water alone was abandoned, and it was decided to

[1] THIS JOURNAL, 38, 175.

maintain the water in the bath at a temperature slightly *above* that of the water circulating in the pipes. The heating, according to the plan developed along this line, was accomplished and controlled by submerged electric stoves and thermostats. The beneficial results of the new scheme were immediately apparent. Four new series[1] of measurements, comprising 80 determinations of osmotic pressure, have been finished since it was put in operation. In 53 of these, there was no sensible change in temperature while the cells were in the bath; in 17 experiments, it amounted to 0°.1 or less; in 7, the variation was 0°.2 or less; while in three it did not exceed 0°.3. The plan was not immediately perfected, hence fluctuations of bath temperature occurred more frequently, and were larger, in the earlier work. The details of the new arrangement were gradually improved and finally brought into such a highly satisfactory state, in nearly every respect, that, throughout the last of the four series, there was not any sensible variation in bath temperature.

The account of the present improved methods of regulating temperature would be incomplete without a sketch of the earlier attempts to maintain an equality of temperature in the water of the bath and in the enclosed air space above. It is manifestly desirable, though it is not absolutely necessary, that the solution in the cell, which is submerged in the water, and the gas in the manometer, which is in the enclosed air space, shall have the same temperature. There are, however, certain very obvious difficulties in the way of securing and maintaining this condition. The water, by virtue of its enormous capacity for the absorption of heat without much change in temperature, is only slowly affected by external conditions, while the enclosed air is very sensitive to them. Moreover, it is impracticable, in a structure which, like the enclosure over the water bath, must be frequently opened, to make the joints gas-tight. Hence the air within is constantly escaping, while the outer air is as constantly entering the enclosed space.

At the outset, the walls surrounding the air space were

[1] This Journal, **39**, 667; **40**, 1, 194, and 325.

made as nearly tight and as completely nonconducting as possible, and the hinged front and top were made to close against rubber weather strips; and during a measurement, the joints were covered externally with surgeon's adhesive tape. But the provision from which most was expected was the forced circulation of the air through pipes lying in the water. Four series[1] of measurements were carried out before introducing any decided improvements in the original scheme for keeping a uniform temperature in the two sections of the bath. The following table will show for each series the number of readings made, the greatest and least observed difference between the temperature of the water and that of the air, and the average of all the differences.

Table II.

Series.	Number of readings.	Greatest difference.	Least difference.	Average of all differences.
I.	100	2°.50	0°.00	0°.53
II.	90	1°.90	0°.00	0°.44
III.	137	1°.65	0°.08	0°.68
IV.	83	0°.91	0°.30	0°.60

The success of the attempt to maintain the equality of temperatures in question is best judged by the averages in the last column. The "greatest" differences are of little significance, as they were usually due in large measure to the necessity, which occasionally arose, of opening the bath during an experiment; in other words, to temporary causes. Series I. and II. were carried out at room temperature, while III. and IV. were made at temperatures close to 0°. This will explain why the averages of the second pair are higher than those of the first, since the difficulty of maintaining the enclosed air at the temperature of the water in the bath obviously increases with the difference between the temperature of the latter and that of the external air.

The circulating system of pipes for hydrant water previously mentioned was next introduced into the bath for the purpose of securing several intermediate temperatures, and

[1] This Journal, **36**, 1; **37**, 324, 425, and 558.

an attempt was made to measure the osmotic pressure of cane sugar solutions in the vicinity of 5°.0. But the temperature of the hydrant water soon rose above 5°.0, and it was frequently necessary to employ small quantities of ice, both in the water and in the enclosed air space. This could be done fairly successfully in the case of the water, but the introduction, even of small quantities, of ice into the air space often produced considerable and irregular changes of temperature. As regards the maintenance of equal temperatures in the two divisions of the bath, *i. e.*, in the water and in the air space, this series is to be regarded as less satisfactory than any which preceded or followed it, though in some other, more essential respects, it was better than any previous one. The following tabular statement presents the number of readings, the greatest and the least observed differences between the temperature of the water and that of the enclosed air, and the average of all the differences:

Table III.

Series.	Number of readings.	Greatest difference.	Least difference.	Average of all differences.
V.	79	5°.05	0°.63	1°.47

Later, a number of improvements were gradually introduced with a view to securing greater constancy of temperature in the water, and at the same time greater uniformity of temperature in the two divisions of the bath. The character of these improvements will be made clear in the latter part of this paper. For the present, it is only necessary to show, by means of the following table, how far they have contributed toward the second object. The statement concerns the last four series of measurements, *i. e.*, those which have been made since the submerged electric stove and thermostat mentioned above were first introduced into the water of the bath. Here again, the results should be judged, not by the "greatest" differences, which are of an accidental and temporary character, but by the means of all the observed differences in temperature:

Table IV.

Series.	Number of readings.	Greatest difference.	Least difference.	Average of all differences.
VI.	63	1°.40	0°.20	0°.68
VII.	56	1°.80	0°.00	0°.67
VIII.	67	1°.50	0°.00	0°.49
IX.	80	0°.60	0°.00	0°.12

In the last series (IX.), the average of all differences was only 0°.12, and this is a fair measure of the agreement between the temperature of the water and that of the air above it which we are able to maintain with our present arrangements.

The introduction into the bath of a system of pipes through which the hydrant water was made to circulate, and, later, of electric heaters and thermostats which were submerged in the rapidly moving water surrounding the pipes, led, in a short time, to the elaboration of a general scheme for water bath regulation. The central idea of the system may be stated as follows: *If the water in any bath is made to pass rapidly* (1) *over a continuously cooled surface, then* (2) *over a heated one which is more efficient, but under the control of a thermostat, and* (3) *again over the cooling surface, etc., it should be practicable to maintain in the bath any temperature for which the thermostat is set, and the constancy of the temperature should depend only on the sensitiveness of the thermostat and the rate of flow of the water.* The principle is a general one and provides for the maintenance of any temperature between 0° and the boiling point of water. Moreover, any desired temperature can be maintained without regard to the temperature of the surrounding atmosphere, since the air about the bath must always aid either in the work of the cooling surface or in that of the heating surface, according as its temperature is lower or higher than that which is being maintained in the bath.

We shall now attempt to show how the principle stated above has been utilized in our most recent work upon osmotic pressure; and, first of all, we shall describe, not the bath in which the measurements are made, but that in which the solu-

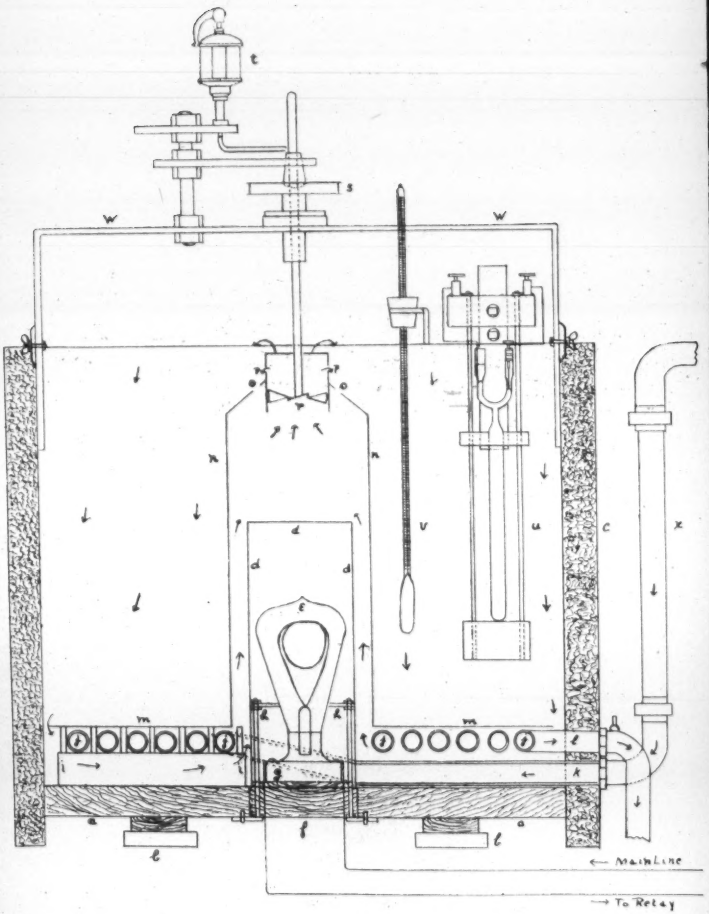


Fig. 1.

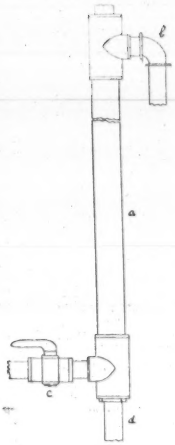


Fig. III.

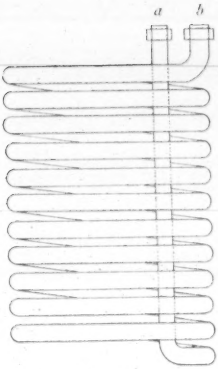


Fig. IV.

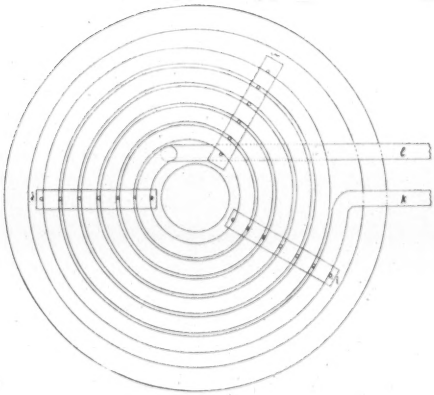


Fig. II.

tions are brought to the required temperature before filling the cells, and in which, also, the cells are kept before and after a measurement of pressure. We may also state that in the laboratory the bath about to be described has generally superseded, in one form or another, all other devices for maintaining constant temperature between 0° and 100°.

Fig. I. represents a cross section of a galvanized iron bath holding about 60 liters. It rests upon the wooden base *a a*, which is raised above the table by the blocks and rubber pieces *b b*, and is surrounded by the thick hair pad *c c*. Inverted over a hole in the center, and riveted and soldered to the bottom of the bath, is the cylinder *d d d*, which serves as a receptacle for the lamp *e*, or any other suitable kind of electrical heating device. The hole in the wooden base *a a* is slightly larger than that in the bottom of the bath, and into this is fitted the block *f*, on which is fastened the lamp base *g* and the lamp guard *h h*. The lamp block is held in its place by buttons screwed to the bottom of the wooden base.

Resting upon the framework *i i* (Fig. I.) and *i i i* (Fig. II.) is the continuous block-tin pipe *j j j j*, through which the hydrant water circulates. This furnishes the "cooling surface" previously referred to. The running water enters the bath at *k* and leaves it at *l*. The course of the water in the pipe, after entering the bath, is continuously horizontal or upward—never downward. This arrangement is necessary in order to prevent the lodgment of air in any part of the pipe. The plan of the continuous tin pipe and of the frame on which it rests is seen in Fig. II. The successive coils of the pipe (six in number) are separated by the pegs seen in Figs. I. and II., and on these rests the galvanized iron disc *m m*. The hood *n n* shuts down tightly over a flange on the disc *m m*, and is secured in its place by means of set screws directed towards *d d*. The form of the hood will be clear from the figure, and it is necessary only to call attention to the pin holes, for the escape of air, at *o o*, and to the larger holes at *p p*, through which a portion of the water raised by the propeller *r* escapes into the outer bath.

The propeller *r* is revolved at any required speed by a smooth porpoise-hide belt, six mm. in width, which is passed around the pulley *s*, and over the pulley of a small motor located at some distance from the bath. To prevent vibration, a long belt, supported at intervals by loose pulleys, is used. The wearing parts of the machinery are lubricated from the oiler *t*. The thermostat is seen at *u*, and the thermometer at *v*. The supports for both are clamped to the rim of the bath, as is also the adjustable support *w w* for the propeller and its accessories.

It is quite essential that the hydrant water flowing through the pipe in the bath shall be under a constant pressure; otherwise, much water and heat are necessarily wasted. The arrangement by which the constant pressure is secured is shown in Fig. III. It consists of a large standpipe *a*, with an overflow *b* near the top. The water from the tap enters at the bottom and passes to the bath through *c*, where the flow is controlled by a stop-cock. The circulating water is thus brought under an invariable pressure, and it is possible to regulate the quantity passing through the bath with great exactness and for long periods.

It frequently happens that the temperature of the hydrant water is higher than that at which it is desired to maintain the bath. In such cases, the section of pipe *x*, Fig. I., is removed and replaced by another leading to the coil of block-tin pipe seen in Fig. IV. The water enters the coil at *a* (Fig. IV.) and passes out of it at *b* into the bath. To cool the hydrant water before it enters the bath, the large and well-protected box in which the coil is located is filled with ice. With the aid of the coil, surrounded by ice, it is practicable to maintain quite low temperatures in the warmest weather.

It remains to explain the electrical arrangements for heating the water in the bath. It is important that the metallic surface *d d d* (Fig. I.), over which the water passes in its upward course through the hood, shall be quickly heated and readily cooled; hence all unnecessary material in the space heated by the stove is to be avoided, and the stove itself should be of the lightest kind. For this reason, lamps have

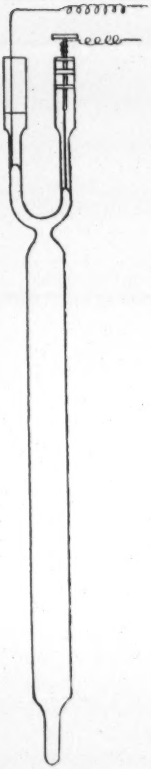


Fig. VI.

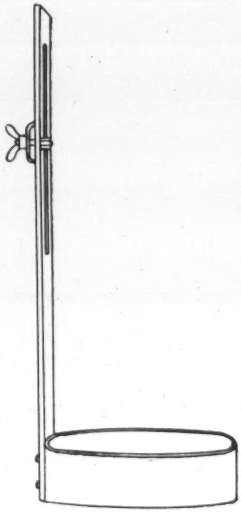


Fig. VII.

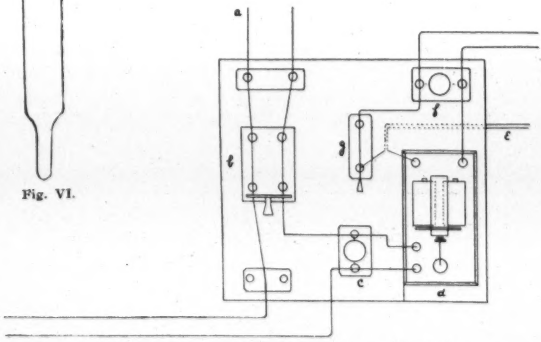


Fig. V.

been preferred to any other variety of electrical heating device. Another great advantage to be gained by the use of lamps is the ease with which, by the selection of lamps with different candle power, the capacity of the stove is suited to the work to be done, *i. e.*, to the temperature to be maintained in the bath.

The arrangement for the regulation of the heater (*e*, Fig. I.) by the thermostat (*u*, Fig. I.) is shown in Fig. V. The main line *a* passes through the switch *b* to the heater *e*, Fig. I. On the return, it crosses one end of the lamp socket *c* and enters the relay *d*. From thence it crosses the other end of the lamp socket and passes through the switch *b*. It will be seen that, whenever the circuit is broken at the relay, the lamp in *c* is thrown into series with the heater *e*, Fig. I., cutting down the current more or less according to the resistance in *c*. The voltage of the current employed is 120, and the resistance in *c* is usually a 240 volt, 16 candle power lamp. The lamp in *c* serves another important purpose. It spans the break in the relay and prevents sparking between the platinum contact points.

The line *e* (Fig. V.) from the single storage cell which operates the relay, after passing through the coils of the instrument crosses one end of the lamp socket *f*, and then passes on to the thermostat *u*, Fig. I. On its return, it crosses the other end of the lamp socket *f*, and passes back to the battery through the switch *g*. The lamp in *f* prevents sparking in the thermostat just as that in *c* suppresses it in the relay. The resistance in *f* should be about 200 ohms, or that of the cold filament of a 16 candle power, 75 volt lamp.

The thermostat is shown separately in Fig. VI. The tube containing the mercury is made larger or smaller, according to the degree of sensitiveness which is required of the instrument. It is also drawn out at the lower end into a smaller tube, which may be broken off and afterwards resealed if it becomes necessary to remove the mercury and cleanse the glass. The narrow tubes in the upper part of the instrument are also varied in diameter according to the requirements of the work. The instrument is filled with mercury until it enters the wi-

dened portion of the two tubes at the top. The end of a platinum wire is buried to a considerable depth in the mercury in one tube, and on the top of the mercury a quantity of dry shellac is placed. The shellac is melted and diminished pressure is applied at the other outlet until the mercury, followed by the molten shellac, recedes well into the narrower portion of the tube, when the shellac is allowed to cool and solidify. The other tube at the top is provided with an adjustable platinum wire, the function of which is sufficiently obvious.

A thermostat of the form just described has the advantage that all of the mercury in the instrument can be submerged in the water of the bath, while the arrangement for adjustment remains above the surface of the water. But the range of temperatures through which it can be used with a fixed quantity of mercury is small. That is, the quantity of mercury must be regulated with reference to the temperature which is to be maintained. This, however, gives very little trouble. If a thermostat is to be employed to maintain a bath at some particular temperature, *e. g.*, 25°, it is plunged —after removing the adjusting screw—into a bath having a slightly higher temperature, and whatever mercury ascends into the wider portions of the tube is removed by means of a very fine pipette. On the other hand, if the mercury recedes too far into the narrow tube, more is added.

We mentioned in an earlier paper[1] the method of suppressing sparking in the thermostats and relays by spanning the spark gap by a resistance bearing a definite ratio to the voltage of the current. The device has proved to be a very useful one, and it is employed in all of our numerous arrangements for the regulation of temperature. It has been found, however, that the desired end, *i. e.*, the suppression of sparking, is much more readily accomplished if the necessary resistance is spread over a large surface. Accordingly, in the large permanent bath, the spark gaps of the thermostat are spanned, not by lamps, but by porcelain tubes which were evenly painted with a mixture of bolted clay, finely pulverized graphite, and a little soap, until the proper resistance

[1] This Journal, **38**, 14.

had been secured. This is the same mixture which was recommended in a former paper[1] for the preparation of heating surfaces of various kinds, and it is especially adapted to the purpose of spreading any required resistance uniformly over any area of surface.

Notwithstanding the suppression of all visible sparking, the mercury in the narrow tube of the thermostat becomes somewhat stiff, after a time, and the instrument begins to respond less promptly to minute changes in temperature. Whenever a symptom of this kind is detected, the thermostat is placed in a bath of higher temperature, and the mercury which rises into the enlarged portion of the tube is removed and replaced by fresh metal.

It may not be out of place to mention here a new kind of thermostat of extreme sensitiveness, in which mercury contact is avoided. We shall only explain the principle on which it is constructed because some of the mechanical details have not yet been perfected. The principle in question is that of a balance, in which two glass bulbs connected by a nearly capillary tube play the part of the beam. One of the bulbs is closed, except for the opening into the glass tube, while the other bulb has attached to it a short open tube. The closed bulb and the connecting tube are filled with mercury, and a quantity of mercury equal to that in the closed bulb is put into the slightly more capacious open one. It will be seen that if an arrangement of this kind is placed upon a knife edge in such a position that the center of gravity is slightly below the point of suspension, we shall have a sensitive temperature balance; for any change in the volume of the mercury, in effect, transfers a portion of the metal from one end of the beam to the other, and the difference in the weight of the two ends, which is thus produced, is double that of the mercury transferred. The instrument is provided with means for adjusting the distance between the point of suspension and the center of gravity, according to the degree of sensitiveness required, and also for equalizing the weight of the two arms of the beam. The circuit is opened and

[1] THIS JOURNAL, **32**, 93.

closed by means of the "pointer." Such an instrument must, of course, be adequately protected against currents of air or water.

Fig. VII. represents the support for flasks, etc., which is used in the bath. It is clamped to the rim of the bath, and, as will be seen from the figure, it can be depressed to any required depth in the water. The bottom is perforated to permit the rapid passage of water. Each bath of the size represented in Fig. I. will accommodate five such supports in addition to the thermostat and thermometer.

The use of the bath is very simple. The thermostat is adjusted to close the circuit at the temperature at which the bath is to be maintained. The bath is brought nearly to that temperature by means of hot water, or ice, or by passing a current of hydrant water through the coiled pipe in the bottom. The flow of hydrant water—cooled, if necessary, by first passing it through the ice coils (Fig. IV.)—is then so regulated that it will very slowly lower the temperature of the circulating water in the bath. The rate of the lowering need not exceed 0°.25 per hour, and it should be, for reasons of economy, as small as it is possible to make it. The lamp which is employed as a heater is selected with reference to the temperature to be maintained. It is only necessary that it shall be able, by burning all the time, to raise the temperature of the bath somewhat faster than the running hydrant water is able to lower it. The thermostat will then permit the lamp to burn only as much of the time as is necessary to maintain the temperature for which the instrument is set.

The water, as it reaches the top of the hood, after passing over the heating surface, is symmetrically distributed towards all sides of the bath, giving a uniformity of temperature throughout the bath which is very satisfactory.

The maintenance of any temperature from a little above 0° to that of the room can be readily accomplished by means of the hydrant water, with or without ice. If, however, a temperature above that of the room is to be maintained, the flow of the hydrant water is cut off. The outer surface of the bath and the free surface of the water then become the

"cooled" surface, and the bath works on precisely the same principle as when hydrant water is made to circulate through the tin pipe in the bottom. If a temperature above 50° is to be maintained, the consumption of electrical energy becomes expensive in large baths, and it is well to accomplish a portion of the heating by other means. This is done in various ways, the simplest of which is to remove the wooden base and place a gas stove under the bath, taking care so to regulate the quantity of burning gas that the stove *alone* cannot raise the temperature of the bath to the required height. It is only the remainder of the work which is then accomplished by the electrical heater. Another method of economizing electrical energy, when high temperatures are to be maintained, is to cause hot water to circulate through the pipe in the bottom of the bath, using for the purpose a device constructed on the principle which is employed in house heating by hot water. Here again, the work which the auxiliary heater is allowed to do must be less than the required maximum, so that the final regulation of temperature may always fall to the electrical devices.

It may be of interest to learn how closely bath temperatures may be regulated by the means here described. We can say, in general, that the variations can not ordinarily be detected on thermometers which are graduated to tenths of a degree and which can be read to hundredths. In the case of one bath of 60 liters capacity, in which a temperature of 25° was being maintained, we took the trouble to ascertain definitely the range of temperature within which the thermostat would open and close, or close and again open the lamp circuit. It was found to be 0°.002.

The same principles are employed in regulating the 300-liter baths in which the measurements of osmotic pressure are made. It will, therefore, be necessary only to mention certain peculiarities in the arrangements for this part of the work. The system of pipes which was first introduced into the bath for the purpose of circulating the hydrant water proved to be unsatisfactory in one way. The pipes, as explained in the earlier part of this paper, were placed *vertically*

around the sides of the bath, with the lower ends under the water and the upper ends in the air space above. The obvious purpose of the arrangement was to maintain an equality of temperature in the two sections of the bath. The difficulty which arose was one which should have been foreseen. The gas which was expelled from the circulating hydrant water, in consequence of rising temperature, collected in the upper ends of the tubes to such an extent that it was frequently necessary to "flush out" the whole system; and this brought about changes in the temperature of the bath which could not be tolerated. Accordingly, the vertical pipes were removed, and in their place was introduced a circulating system which will be briefly described. Supported on an open framework near the bottom of the bath is a series of connected horizontal brass pipes with an aggregate length of 10 meters. This collection of pipes is the analogue of the coiled block-tin pipe in the bottom of the bath previously described. The hydrant water enters it, from the pressure regulator, at the lowest point and passes through the succession of pipes, always in a horizontal or upward direction, thence through a vertical pipe to the air space above. The vertical pipe here connects with a second system of horizontal pipes, placed one above another, which is fixed to the walls of the air space; and the water, after circulating through this, enters a third system of horizontal pipes which is suspended from the top of the bath. There is no opportunity for the lodgment of gas in any part of the course taken by the water, hence it is practicable to regulate the flow with considerable exactness. If necessary, the hydrant water is cooled, before entering the bath, by passing it through a coil of pipe surrounded by ice. The slowly circulating water, while passing through the pipes lying in the bottom of the bath, is warmed nearly to the temperature of the bath water, and it may not, on that account, be able, while passing through the upper portion of the system, to keep the temperature of the air space low enough; hence provision is made for reinforcing the stream with an additional quantity of cold water while it is running through the upper part of the bath.

In the large bath, as in the smaller one represented in Fig. I., the water is pumped first over the cooled surface, *i. e.*, over the pipes near the bottom, and then over the heated surface. Each of the baths is provided with two stoves, either one of which may be operated independently of the other, though both are under the control of the same thermostat. Fig. VIII. shows one of the stoves enclosed in a galvanized iron tube. The stoves are located in the end of the bath which is not covered by the superstructure, and they are, therefore, accessible from the outside.

The arrangements as described are satisfactory in respect to the maintenance of constant temperatures in the lower section of the bath, *i. e.*, in the water in which the osmotic cells are placed for a measurement of pressure, but they were found to be insufficient to maintain the same temperatures in the upper section, *i. e.*, in the air space in which the upper ends of the manometers are located. Even the rapid pumping of the air in this section through pipes lying in the water, and the introduction of a small fan—propelled from the outside—to agitate the air, did not fully neutralize the effect of external conditions. It was therefore decided to bring these external conditions under better control by making the necessary provisions for keeping, outside of the bath, approximately the same temperature as we were endeavoring to maintain on the inside.

The bath, as stated in an earlier part of this paper, is located in a small room, 3.3 meters in length, 2 meters in width, and 2.6 meters in height. It was this space which was to be automatically heated or cooled, according to the demands of the work going on inside the bath. We shall first describe the cooling device. It consists of a series of galvanized iron pipes, having a total length of 100 meters, through which the hydrant water—cooled by ice, if necessary—may be made to flow at any required rate. One-half of the pipe, namely, 50 meters, is suspended from the top of the room in parallel lengths equal to the length of the room itself. These pipes have a diameter of about 50 mm. and present, therefore, a large cooling surface. The remainder of the pipe (50 meters)

is smaller (25 mm. in diameter), and is cut into 2 meter lengths, which are compactly arranged in a large ice box. The water enters the ice box directly from the main supply, and, after passing through the series of short pipes in the box, it ascends through a vertical pipe to the system of symmetrically distributed large ones in the top of the room.

There are two varieties of heating devices in use. One of these consists of two small electric stoves, which are situated outside the bath but are controlled by a thermostat *within* the air space. The other heating arrangement is a gas stove controlled by a thermostat which is located on the *outside* of the bath. The purpose of the gas stove is simply to economize electrical energy, and it is used only when a considerable supply of heat is necessary. It is never allowed to furnish all the heat required, and that it may not do so, its thermostat is set for one or two degrees below the temperature which is to be maintained in the bath. The final regulation of the temperature of the little room is thus always left to the electric stoves, which, being under the control of a thermostat within the enclosed space, can burn only so much as is necessary to keep the temperature of the space up to that of the water in the bath. The air in the room is kept in constant circulation by a motor fan which is located with a view to keeping the temperature of all parts of the room as uniform as possible.

With these facilities for cooling and heating, we are now able to maintain a variety of constant bath temperatures without much regard to the season of the year; nevertheless, it is advisable, on economical grounds, to do the work at low temperatures in winter and that at higher temperatures in summer. It will be seen that the problem to be solved is the same in every case, namely, to regulate the cooling devices so as to produce, both within and without the bath, a temperature somewhat below the one at which the work is to be done, and then to leave the differences to the automatic heating devices.

The gas regulator which is used with the stove is perhaps

Fig. VIII.

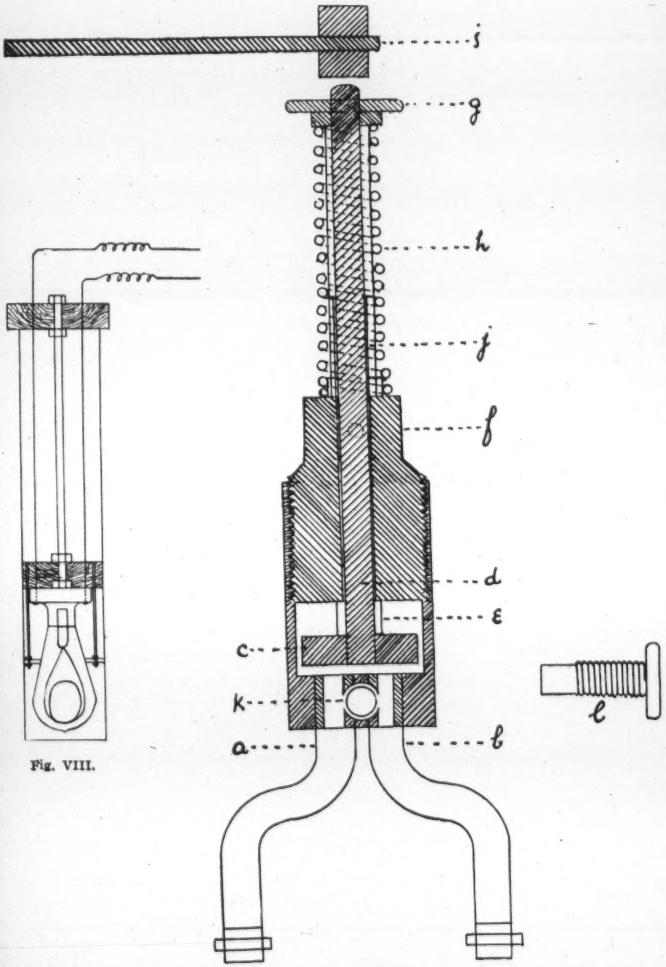


Fig. IX.

worthy of a description. In a former paper[1] we gave an account of a gas regulator in which the flow of the gas is controlled by an iron ball, which is raised into place and dropped again by the closing and opening of the circuit of an electromagnet. The instrument, when correctly made, was a satisfactory one except in one particular. It was found very difficult to obtain perfectly spherical balls of sufficiently pure and soft iron. All of those which were used became, after a time, permanently magnetized to such an extent as to render the regulators unreliable. They were therefore abandoned for the form of regulator which is shown in Fig. IX. It is made entirely of brass and is connected directly—*i. e.*, without the intervention of rubber tubing—on the one side to the gas supply pipe, and on the other, to a metal tube leading to the stove. The two pipes *a* and *b* through which the gas flows are closed and opened by the disc *c*. Above the disc, upon the rod *d*, to which it is attached, is the soft rubber ring *e*. The distance through which the disc *c* may move is regulated by the threaded plug *f*, through which the rod *d* passes. Above the plug *f* is the spiral spring *h*, the strength of which can be regulated by the nut *g*. The spring raises the disc *c* and permits the gas to pass from pipe to pipe, as long as the hammer *i* is raised; but when the hammer descends, the disc is driven down upon the open ends of the pipes, shutting off the gas. The hammer is worked by an electro-magnet, which is under the control of a thermostat, and it remains down, stopping the flow of gas, as long as the circuit is closed. To prevent a possible escape of gas into the room, a thin, very flexible rubber tube *j* is slipped over the rod *d* and over a short metal tube projecting from the upper end of *f*. The two pipes communicate also through the hole *k* and the amount of gas which may take this course between the pipes is regulated by the screw *l*.

JOHNS HOPKINS UNIVERSITY,
December 15, 1908.

[1] THIS JOURNAL, **38**, 18.

ON THE RELATIVE EASE OF ADDITION IN THE ALKENE GROUP.

[FIRST PAPER ON THE LAWS OF ADDITION IN ORGANIC CHEMISTRY.]

By Arthur Michael and Roger F. Brunel.

In organic chemistry numerous attempts have been made to formulate empirical laws to apply to addition phenomena. Markonikoff,[1] who first noted a regularity in the addition of halogen acids to unsaturated hydrocarbons, laid down the rule that the halogen in such cases goes to the carbon joined to fewer hydrogen atoms, *i. e.*, to the one most under the influence of other carbon atoms. A few years later it was shown by Saytzeff[2] that this rule was not general even for alkenes, since it was found that in the addition of hydriodic acid to unsymmetrical ethylmethylethylene the halogen unites with the unsaturated carbon which, from the Markonikoff point of view, is less under the influence of other carbon atoms,[3] and Linnemann[4] showed that it was not valid for unsaturated organic acids, as in the union of halhydric acids with acrylic acid the halogen unites with the methylene and not, in accordance with the principle involved in the Markonikoff rule, with the methine group.[5] In 1887 one of us[6] showed that a general law of addition, not only comprehending the various classes of unsaturated organic derivatives but connecting the course of the process with the structure of the substances, could be based on the "positive-negative" hypothesis. It is safe to say, however, that an empirical law cannot be formulated to which exceptions will not be found, and we shall give here a brief outline of the subsequent development[7] of the "posi-

[1] Ann. Chem. (Liebig), **153**, 256 (1870).

[2] *Ibid.*, **179**, 296 (1875).

[3] Compare Michael: J. prakt. Chem., N. F., **60**, 348 (1899).

[4] Ann. Chem. (Liebig), **163**, 96 (1872).

[5] Later Hemilian (*Ibid.*, **174**, 326) and Fittig and his pupils (*Ibid.*, **188**, 42; **195**, 56) endeavored to prove that with other acids of this series α-halogen derivatives are formed, but Erlenmeyer, sen. (Ber. d. chem. Ges., **13**, 394) and Michael and Freer (J. prakt. Chem., N. F., **40**, 96) showed that β-substituted acids are really formed.

[6] Michael: J. prakt. Chem., N. F., **37**, 524.

[7] Michael: *Ibid.*, **60**, 341-351, 443-470; **68**, 499; Ber. d. chem. Ges., **39**, 2139, 2143, 2157.

tive-negative" law of addition, which is universal since it is founded on the principle underlying all chemical phenomena, *i. e.*, the law of entropy.

The second law of thermodynamics demands that all spontaneously occurring chemical changes shall be accompanied by an increase in the entropy of the system. Furthermore, we know that where several courses are possible for a reaction the *tendency* is to follow that by which the greatest increase in entropy will result; while, the nearer together the entropy changes in the different directions lie, the more nearly equal become the amounts of the corresponding products obtained[1]—a more fundamental and general statement of the partition principle first suggested by Thomsen[2] in connection with his investigations on the avidity of acids. To establish a more direct connection in the change of any chemical system between the change in entropy and the constitution of the compounds that may be formed, we may start from the assumption that the more nearly complete the neutralization of the chemical forces in the new chemical system, the greater will be the entropy.[3] It follows from such a relation that the tendency of any unsaturated organic substance, in passing over into a more saturated derivative, is to give rise to a substance whose structure or configuration represents the maximum chemical neutralization of the atoms. This neutralization principle has been expressed by one of us as follows: "In any chemical reaction the total energy of the atoms involved is the more completely converted into bound energy and heat, the more nearly the chemical forces in these atoms are able to neutralize each other."[4] In an organic substance which represents a very complete state of intramolecular neutralization, the energy of each atom is largely expended through direct union or through space in holding in combination the other atoms of the molecule, and the portion of the energy so expended is here designated as *bound chemical* energy. In as far as the chemical forces in the molecule are

[1] Michael: J. prakt. Chem., N. F., **60**, 340; Ber. d. chem. Ges., **39**, 2138.
[2] Pogg. Ann., **138**, 497.
[3] Michael: J. prakt. Chem., N. F., **68**, 489.
[4] Michael: *Ibid.*, N. F., **60**, 292; Ber. d. chem. Ges., **38**, 23.

not so neutralized, some of the atoms will still be able to exert attraction toward such other atoms as they have an affinity for in the same or other molecules, and this portion of the energy, not used directly or indirectly through union with the rest of the atoms of the molecule, is designated as *free*[1] *chemical* energy. When the chemical forces of opposite character[2] in the molecule are nearly equal, neither the molecule as a whole nor any of its atoms can exert much attraction towards other molecules. There can be but little free chemical energy present in such a molecule and the substance will be comparatively stable and, in general, chemically inactive.[3]

It is now necessary to see what connection there is between these principles and the velocity of chemical reactions. It is assumed that the first step in every chemical reaction is the formation of an intermediate "Kekulé double molecule."[4] The velocity with which the reaction takes place will depend largely on two factors: first, the attractive force between the reacting molecules, which determines the ease with which the double molecule will be formed, and depends on the amount and nature of the free *chemical* energy present;[5] second, on the increase in entropy brought about by the reaction, which is a large factor in determining the tendency of the double molecule to rearrange to give the resulting substances. The fact that in the cases where different products may be formed the reaction does not always lead at once to the formation of those which would represent the highest degree of entropy

[1] The terms free and bound *chemical* energy, as here used, are not to be confused with the terms free and bound energy as used in physical chemistry, with which they are not identical.

[2] These forces of opposite chemical character are often designated as positive and negative. These terms are confusing, since they bring to mind some sort of electrical conception. Although they sometimes coincide with the electrochemical character of the atoms or radicals in question, there is no inherent connection with these, the terms being merely relative, and used to designate kinds of chemical energy which act differently from each other.

[3] For further details regarding the application of these principles see Michael: J. prakt. Chem., N. F., **68,** 488; This Journal, **39,** 1; Ber. d. chem. Ges., **39,** 2139-2163; **41,** 2907; Ann. Chem. (Liebig), **363,** 21-106; **364,** 64.

[4] Kekulé: Ann. Chem. (Liebig), **106,** 141. Michael: Ber. d. chem. Ges., **34,** 4028; **39,** 2140; This Journal, **39,** 3.

[5] The two factors that permit a chemical change, *i. e.*, free chemical energy and chemical affinity, have together been designated chemical potential (see Michael: Ann. Chem. (Liebig), **363,** 21).

of the system must be attributed to intramolecular resistance of some sort, due sometimes to the difficulty in overcoming the bound *chemical* energy existing between certain atoms. The *chemical* potential of the atoms is not always sufficiently strong to overcome this intramolecular resistance to the formation of the structure or configuration representing the maximum entropy of the system.[1]

A typical example of the application of these principles to organic chemistry is to be found in the addition of halogen acids to unsaturated hydrocarbons. Here free *chemical* energy is always present in considerable amount in the hydrocarbon, the question being whether it is of such a nature as to attract the hydrogen and halogen of the addendum. Furthermore, when the addition leads to the formation of isomeric products, the breaking down of an alkene-halogen acid double molecule involves no rearrangement of atoms already joined, except the separation of hydrogen and halogen, which is the same for both of the possible isomers, so that the relative amounts of the products may be assumed to be dependent only on the entropy of the two reactions.[2] The question as to whether such an addition will take place, and as to which of two possible isomers will be formed (or, if both, in what ratio) will depend on the possible extent of neutralization of both the hydrogen and halogen in the molecules of the addition products that may be formed.

The idea, first suggested by van't Hoff,[3] that the influence which two atoms in a molecule exert on each other is to be divided into two parts—first, direct, acting through direct union or through space; second, indirect, exerted through the intermediate atoms—has been further developed[4] and shown

[1] See Michael and Bunge: Ber. d. chem. Ges., **41**, 2908.

[2] While it cannot be stated at present just how near the relative amounts of isomers formed in the addition reactions here under consideration come to those demanded by the entropy of the reactions, there is certainly an approximate agreement (see Michael: THIS JOURNAL, **39**, 6; Ber. d. chem. Ges., **39**, 2140-2163; J. prakt. Chem., N. F., **68**, 499). It is apparent that we can consider from the above point of view only reactions where the states of aggregation of the systems before and after the chemical change are so similar that the entropy factors arising from these causes may be eliminated.

[3] Ansichten, I., 284; II., 252.

[4] Michael: J. prakt. Chem., N. F., **60**, 331; Ber. d. chem. Ges., **39**, 2138-2157 and 2780-2790; **40**, 140.

to be of great importance in enabling us to understand organic reactions. If in an aliphatic compound with normal chain a certain carbon atom be designated by the figure 1, our present knowledge of the mutual influence between this atom and others in the molecule is best expressed by the following scale, the numbers indicating degree of removal from the atom in question and the strength of the influence decreasing in the order given:[1]

2–3–5–6–4–7–(9–10–11)–8.

It is to be strongly emphasized that the effect of an atom not far removed, *i. e.*, in position 2 or 3, whether it is direct or, if indirect, lessened by the interference of only one atom, is far greater than that of any similar atom less closely connected; and that in the case of atoms farther removed the influence must be largely direct, *i. e.*, spatial. By numbering the atoms as above and summing up the influences acting on the two unsaturated carbon atoms of an alkene hydrocarbon, we can ascertain the relative degree of neutralization of the halogen and hydrogen atoms of the adding acid in the two isomeric addition products which may be formed. We shall then know more or less closely the relative increases in entropy which would result from the formation of the two isomeric compounds, and this, in connection with the principle of partition, will determine the relative amounts formed,[2] it being assumed, as stated above, that here the intramolecular resistances are equal in each case; while if the increase in entropy is much greater for one than for the other, the latter will not be produced in appreciable quantity, although we must assume that in all cases both possible isomers are formed.[3]

How structural changes in the compounds concerned may affect the relative amounts of isomers formed has been already

[1] J. prakt. Chem., N. F., **60**, 335.

[2] This has been shown experimentally in the addition of hydriodic acid to 2-hexene (Michael and Hartman: Ber. d. chem. Ges., **39**, 2149) and of water to 2-hexine (Michael: *Ibid.*, **39**, 2143).

[3] This was proven in the case of addition of hydriodic acid to propylene (see Michael and Leighton: J. prakt. Chem., N. F., **60**, 466).

discussed and examined experimentally by one of us.[1] The point of primary importance in this paper is the relative additive power of different alkenes.

To consider the case most generally from a theoretical standpoint, let us represent any compound containing an ethylene grouping $\cdot(C:C)$ by the formula $\overset{X}{\diagup\diagdown}C:C$,[2] including under X all the rest of the molecule, and assuming for the present that its effect on the two carbon atoms is practically the same. We may imagine in the first place that X is of such a nature that while the resulting power of the unsaturated carbons to unite with hydrogen is great they have little capacity to combine with halogen. The entropy change, when the second stage of the addition takes place, that is, when the double molecule changes over into an ordinary molecule, is the sum of three quantities: the change involved in separating hydrogen from chlorine (negative) and those involved in the union of these with the two carbon atoms (positive). If the last two together are greater than the first, the addition may take place, for the neutralization will be greater after it does; otherwise, it could not spontaneously occur. In the case above described, the energy of chlorine would be so much less completely neutralized in combination with carbon than in hydrochloric acid that a greater degree of entropy is represented by $\overset{X}{\diagup\diagdown}C=C + HCl$ than by $X\begin{cases}C—H\\ |\\ C—Cl\end{cases}$. In such a case

[1] Michael: J. prakt. Chem., N. F., **60**, 345-351 and 445; **68**, 499; Ber. d. chem. Ges., **39**, 2141 and 2143. Exceptions to the Markonikoff rule have from time to time been found and some of these have already been discussed by one of us and explained according to the principles stated above. One recent very interesting instance may be mentioned here. Delacre (Centralb., **1906**, I., 1233) found that hydriodic acid adds to tertiary butylethylene to give a primary, instead of the expected secondary, derivative. This exception to the Markonikoff rule is attributed to "unexplained influences." The nine hydrogen atoms of the tertiary butyl group are, however, in the 4-position to the β and the 5-position to the α unsaturated carbon atom, and the much greater influence of atoms in the latter place could leave no other result to be expected than the union of the halogen to a very considerable extent with the α carbon atom. Since, however, the determining forces here are all those of atoms not directly connected with the unsaturated carbons, the product of the addition should contain also the secondary iodide in appreciable quantity (see Ber. d. chem. Ges., **39**, 2141).

[2] This is not intended to represent a ring compound.

spontaneous decomposition of the latter compound would be possible, if the attraction between hydrogen and chlorine were sufficient to overcome their union with the carbon atoms.

But we may alter the character of X so that the affinity of carbon for chlorine will increase. This will be the result if X contains atoms which themselves have an affinity for chlorine, in the present case hydrogen atoms, but this will at the same time decrease the tendency of the carbon to unite with hydrogen.[1] Nevertheless, addition may now occur, *i. e.*, such addition would be accompanied by increase of entropy.[2]

The tendency to add will increase as we continue to alter the character of X in the same direction. This will hold, however, only to a certain point, for we are decreasing the power of the unsaturated carbons to unite with hydrogen, so that after a point of relatively great additive power is passed, we shall again approach a point where addition cannot take place spontaneously, this time because, while the affinity for the chlorine is great, the union of carbon with the hydrogen of the adding acid will represent so slight a degree of neutralization that a higher degree of entropy will again be found in the system $\begin{matrix} X \\ \diagup \\ C = C \end{matrix} + HCl$. Here, again, the compound $X\begin{matrix} C{-}H \\ \diagup \quad | \\ \diagdown \quad | \\ C{-}Cl \end{matrix}$, if formed under certain conditions, might decompose spontaneously at ordinary temperature.

In the alkene series X consists of carbon and hydrogen atoms. Since additional carbon atoms have much less effect on those already present than atoms of a different character,

[1] Carbon in itself has an affinity for hydrogen and for the halogens and other nonmetallic atoms as well, but the degree of this affinity can be considerably affected by other atoms present in the molecule. Carbon and hydrogen are chemically remarkably plastic, *i. e.*, their affinity relations are very sensitive to the influence of other atoms (van't Hoff: Ansichten über organ. Chem., I., 280; II., 242; Michael: J. prakt. Chem., N. F., **60**, 325). With increasing influence of hydrogen on an unsaturated carbon, its chemical character tends to become more and more like that of more metallic elements. Such changes must therefore increase the affinity of the carbon for halogen, but decrease it for hydrogen (see J. prakt. Chem., N. F., **60**, 290 and 326; Ber. d. chem. Ges., **39**, 2192).

[2] This would not, of course, mean that it would in general occur, but with the alkenes, since large amounts of free *chemical* energy are always present, we may safely assume that it will occur if this energy is of the required character.

i. e., the hydrogen atoms, we need take only the latter into consideration in the present case. On account of the affinity of hydrogen for chlorine we should expect the presence of hydrogen atoms in the molecule to increase the power of carbon to combine with the chlorine so that, in successive members of the series, the latter is constantly becoming more completely neutralized. But toward the hydrogen of the hydrochloric acid, the affinity of the carbon must be lessened by the influence of an increasing number of hydrogen atoms already present in the molecule. Data for the first three members of the aliphatic series have long been available, showing that the additive power toward acids increases as we go up the series, but for the reasons given above it could be stated with certainty that at some point a maximum[1] must be reached, beyond which the neutralization of the hydrogen would be so incomplete that the additive power would become less and less, and, if the series could be continued far enough, might reach zero.

This occurrence of a maximum in additive power may be considered the second part of the fundamental law governing addition phenomena, and will always appear when the addendum consists of hydrogen and a relatively negative atom or group.[2] Examples of this relationship are not wanting in both inorganic and organic chemistry.

In the case of the ammonium and phosphonium compounds, etc., the failure to take this principle into account has caused considerable confusion between *tendency to dissociate* and *basicity* of the radicals.[3] Ammonium chloride is a fairly stable substance, but if the nitrogen be successively replaced by phosphorus, arsenic, and antimony, compounds result which, with increasing *metallic* character of the element, so greatly decrease in stability that phosphonium chloride exists only at —30° and the corresponding arsenic and antimony compounds have never been isolated. This does not,

[1] It is possible that two alkene hydrocarbons with practically the same additive power exist, but our present knowledge does not tend to confirm this view.

[2] See Michael: Ber. d. chem. Ges., **38**, 28. Michael and Cobb: Ann. Chem. (Liebig), **363**, 68.

[3] See Michael and Leighton: Ber. d. chem. Ges., **39**, 2792.

however, justify the conclusion that the AsH_4 and SbH_4 are less basic than the PH_4 and NH_4 radicals, for the stability of these chlorides does not depend on their basicity, but on the question whether a greater degree of neutralization is found in the union of hydrogen with chlorine, or in that of hydrogen and chlorine with the group XH_3. As we substitute the more metallic elements for nitrogen, the ability to neutralize hydrogen decreases, and one of the above elements will give to the radical XH_3 a certain affinity for both hydrogen and chlorine, which will cause a maximum degree of stability in the compound XH_4Cl. That element is nitrogen. Substitution of phosphorus, arsenic, or antimony produces a greater tendency to dissociation, but there is no reason to doubt that in stable derivatives of the four radicals (XH_4) those of SbH_4 would show greater power to neutralize chlorine, that is, be more basic than any of the others.[1]

An interesting illustration of the above law in organic chemistry is found in Bredig's[2] research on the conductivities of alkylammonium bases in aqueous solution. Bredig showed that the value of K increases considerably in passing from a mono- to a dialkylamine, but that from the latter to a trialkylamine an almost equally marked decrease occurs. He concluded from these results that the dialkylamines are stronger bases than either the mono- or trialkyl compounds. It is extremely improbable that such an irregularity in the degree of dissociation of the substituted ammonium hydroxides would occur, but it is more likely that they would all be dissociated to a very considerable extent and that the degree of dissociation would increase slightly with the introduction of each additional alkyl group. On the other hand, there is every reason to believe that the conductivity of the alkylamines in aqueous solution depends largely on the proportion of the amine in combination with water as alkylammonium hydroxide, so that Bredig's results only show

[1] The tetramethylhydroxy derivatives of these four elements are known and; although they are all strong bases, there can be no doubt that tetramethylstibonium hydroxide is the strongest and tetramethylammonium hydroxide the weakest base of the series.

[2] Z. physik. Chem., **13**, 289 (1894).

that the dialkylamines unite to a greater extent with water, than the mono- and trialkyl derivatives, *i. e.*, the dialkylammonium hydroxides are more stable than the mono- or trialkylammonium compounds under the conditions of the experiments.[1] Here we notice a similar change in the stability relations. The resultant of the affinity of the compounds $C_nH_{2n+1}NH_2$ for hydrogen and hydroxyl increases with the introduction of a second alkyl radical, but a further repetition of the change decreases that for hydrogen so greatly that a decrease in the stability of the additive product results.[2]

In regard to the additive power of the lower members of the ethylene series the following experiments were already described in the literature. Berthelot[3] showed that ethylene is hardly affected by being heated one hundred hours at 100° with saturated aqueous hydrochloric acid, while propylene is absorbed in seventy hours under the same conditions. Butlerow[4] found that ethylene dissolves readily in concentrated sulphuric acid only at 160°, propylene is acted on at room temperature, while isobutene[5] is absorbed in a short time at room temperature by 50 per cent acid. These facts leave little doubt as to the relative additive power of the three hydrocarbons in question, but later experiments[6] were more satisfactory, as they included a larger number of alkenes and were carried out with dry hydrochloric and hydrobromic acids at the same time and under exactly the same conditions. It was found that ethylene unites less readily than propylene and this less readily than *n*-butene, and, in accordance with the theory,[7] the difference in the velocities between the first is considerably less than between the last-named hydrocarbons. Furthermore, of the isomeric butenes, isobutene unites much

[1] A similar relation has been proven experimentally with the trialkylammonium cyanides. See Michael and Hibbert: Ann. Chem. (Liebig), **364**, 64.

[2] Conductivity measurements of the substituted ammonias in aqueous solution do not represent the relations between the relative basicities of such substances, but those of the relative stability of the corresponding ammonium hydroxides in aqueous solution. An experimental research on this subject will be published later.—A. M.

[3] Compt. rend., **54**, 1350.

[4] Ann. Chem. (Liebig), **180**, 246 (1875).

[5] Ber. d. chem. Ges., **6**, 561 (1873).

[6] Michael: J. prakt. Chem., N. F., **60**, 372 (1899).

[7] *Ibid.*, 373.

more readily than pseudobutene, and the latter somewhat more so than *n*-butene, so that, of the alkenes of the first four series, the additive power is considerably the greatest for isobutene.

That there exists a maximum degree of additive power, with a decrease in the higher members of the alkene series, appeared probable from the observations of Butlerow[1] that diisobutylene adds halogen acids only slowly, and of Kondakow[2] that with hydrochloric acid even heating with the fuming acid in sealed tubes to 100° does not entirely complete the reaction, while the products easily give up the halogen acid. Furthermore, according to Butlerow,[3] triisobutylene seems to add with still greater difficulty and, although it adds bromine readily, the product, as we should expect in accordance with the small affinity for hydrogen, easily gives up hydrobromic acid.

With the object of finding where the maximum of additive power is reached, isobutene, trimethylethylene, tetramethylethylene, and diisobutylene have been investigated. Most of the experiments were carried out with aqueous sulphuric acid, but halogen[4] and phosphoric acids were also used. The expected decrease appeared between isobutene and trimethylethylene, the former being dissolved by aqueous acids in from one-fourth to one-third of the time required by the latter. In passing to tetramethylethylene and diisobutylene the difference in each case is greater than between the first two, as is shown by the figures given below.

Thus, of all the alkenes hitherto examined, isobutene (I.) shows the greatest additive power,[5] and in this compound there exists

[1] Ann. Chem. (Liebig), **189**, 51 (1877).

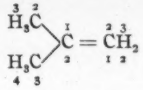
[2] J. prakt. Chem., N. F., **54**, 449 (1896).

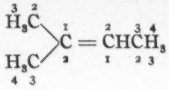
[3] Ber. d. chem. Ges., **12**, 1483 (1879).

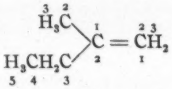
[4] With halogen acids the solutions were dilute enough so that the hydrocarbons added, not acid, but water, giving carbinol. We have investigated this phenomenon and it will form the subject of the second paper of this series.

[5] As far as is known, every alkene is capable of uniting with the usual inorganic addenda, so that additive power coincides here with relative rate in the velocity of the additions. Recalling what has been said above, the velocity of addition with different alkenes may depend on: first, the amount and character of the free *chemical* energy of the unsaturated hydrocarbons; and, second, the increase of entropy brought about by the reaction. It is not possible at present to say what part each factor plays, but that is for the present case unnecessary, since here the two influences work in the same direction. That substance which, through its chemical energy, has the greatest attraction for the two parts of the addendum is the one which will best neutralize their energy by combination.

the greatest difference of polarity between the unsaturated carbon atoms. According to the scale of relative influences given

I. 

II. 

III. 

above, the hydrogen of the two methyl groups is in such a position as to increase to the greatest possible extent the affinity of the β unsaturated carbon for halogen ($\overset{2}{C}\overset{3}{H_3}$), and to decrease least that of the α carbon for hydrogen ($\overset{3}{C}\overset{4}{H_3}$). In trimethylethylene (II.) the additional methyl group is in a position where the hydrogen will affect strongly the carbon with which the hydrogen of the adding acid is to unite ($\overset{2}{C}\overset{3}{H_3}$), and only weakly that to which the halogen goes ($\overset{3}{C}\overset{4}{H_3}$).

In 1877, LeBel[1] described a method for separating the amylenes by means of the differences in their capacity to unite with hydrochloric acid, and also reached the conclusion that only those homologues of ethylene containing the group : CRR′ (that is, those that form tertiary halides in the addition) are attacked readily in the cold. Thus trimethylethylene (II.) and unsymmetrical methylethylethylene (III.) unite more readily than the other amylenes. The difference now found between the additive power of isobutene and trimethylethylene shows that in the series containing 5 carbon atoms the number of hydrogen atoms is already sufficiently great to cause a decrease, and we are now able to account for the difference among the amylenes. Addition takes place readily in this series only where *one* of the unsaturated carbons is joined to two alkyl groups, so that while its attraction for the halogen

[1] Bull. Soc. Chim., **28**, 460. Wischnegradsky (Ann. Chem. (Liebig), **190**, 332) subsequently used dilute sulphuric acid to separate the amylenes, as only those that can pass over into the tertiary carbinol dissolve readily.

is strongly marked, that of the other unsaturated carbon for hydrogen is not correspondingly decreased. The additive power of unsymmetrical methylethylethylene (III.) should be greater than that of trimethylethylene (II.), since the latter adds less easily than isobutene (I.), and the introduction into isobutene of 3 hydrogen atoms in position 5 (relatively to the unsaturated carbon that unites with the hydrogen of the addendum) must decrease the additive power less than when they are introduced in position 3. Methylethylethylene (III.) and trimethylethylene (II.), respectively, are thus related to isobutene (I.).[1]

From the above discussion it is clear that isobutene should possess greater additive power than the other butenes. This would, indeed, be considered very probable merely from the fact that, in adding, it alone forms tertiary derivatives; for the high heat of formation of the tertiary halides and carbinols as compared with the secondary, and of the latter as compared with the primary derivatives[2], is an indication, according to the neutralization principle (p. 119), of the relative condition of intramolecular neutralization in these compounds, and thus of the relative increase in entropy. If we designate the atoms in normal and pseudobutene as above and sum up the influences of the hydrogen, first, on the carbon atoms with which the negative group or atom of the addendum will unite, and second, on the carbon atoms to which the hydrogen will add, omitting such atoms as have exactly or nearly the same value for both, and using parentheses to indicate those hydrogen atoms which are joined directly to unsaturated carbon atoms, as they must have a decidedly less positive effect than those united with saturated carbon, we have the following result:

[1] Whether unsymmetrical methylethylethylene or isobutene possesses the greatest additive power in the alkene series can only be determined by experiment, and we shall try to decide the question in this way.

[2] The rule governing these values has been stated (Michael: J. prakt. Chem., N. F., **68**, 499) as follows: "The heats of formation of aliphatic organic isomers which have a negative organic nucleus in common is proportional to the total influence, *i. e.*, direct as well as indirect, of the positive hydrocarbon radicals on this negative nucleus." Thus, propionic aldehyde and acetone have in common the negative carbonyl nucleus, which, however, is joined directly to the two methyl groups only in the latter substance. This, therefore, has the greater heat of formation.

I. $\overset{5}{H_3}\overset{4}{C}—\overset{3\,4}{CH_2}—\overset{2\,3}{CH} = \overset{1\,2}{CH_2}$. II. $\overset{4\,3}{H_3C}—\overset{2\,3}{CH} = \overset{1\,2}{CH}—\overset{2\,3}{CH_3}$.

Δ^{β}–C of I. : Δ^{β}–C of II. : : $(\overset{3}{H}) : \overset{3}{H}$.[1]

Δ^{α}–C of I. : Δ^{β}–C of II. : : $(\overset{2}{H}) + \overset{5}{H_3}$: : $\overset{4}{H} + \overset{3}{H_3}$.

It is apparent that the influence of hydrogen is somewhat greater on the Δ^{β}–C of pseudobutene (II.) than on the Δ^{β}–C of normal butene (I.), which means that the Δ^{β}–C of pseudobutene has a somewhat greater affinity for the negative component of the addendum than the Δ^{β}–C of normal butene; while the Δ^{α}–C of normal butene, since it is less under the influence of hydrogen than the Δ^{β}–C of pseudobutene, *may* have a somewhat greater attraction for the hydrogen of the addendum. Obviously it is impossible to determine theoretically the relative values of the velocity of addition to these butenes, although it could safely be concluded that the difference between them could not be very great. Preliminary experiments[2] had already indicated that the additive power of the pseudo compound is somewhat greater, and according to the experiments described below, in which dilute sulphuric acid was used as additive reagent, it is nearly twice as great as that of *n*-butene,[3] while the ratio with iso- and pseudobutene is 60–80 : 1.

The hydrocarbons used in this reasearch, with the exception of diisobutylene, were prepared from the iodides by treatment with alcoholic potash. The comparatively low temperature employed makes this method the least likely to cause isomerization. With normal and isobutyl iodides only one alkene is possible, but from the secondary deriva-

[1] In conformity with von Baeyer's suggestion (Ann. Chem. (Liebig), **245**, 112) the capital "Delta" denotes unsaturation: *i. e.*, Δ^{β}–C is the carbon of the CH-group in I. and II.

[2] Michael: J. prakt. Chem., N. F., **60**, 372.

[3] It is assumed here that ordinary pseudobutene (compare Wislicenus, Talbot, and Henze: Ann. Chem. (Liebig), **313**, 228) represents the fumaroid form, which must have a considerably smaller additive power than the maleinoid derivative. When we start from those acetylene derivatives that give stereomeric isomers, we introduce obviously a greater complication in the addition processes, and some facts are known that seem not in accordance with the law of addition. It will be shown later that such apparent contradictions disappear when the reactions are considered from the point of view of the energy relations of the stereomeric products (see THIS JOURNAL, **39**, 1).

tive either 1-butene or 2-butene may result. In 2-iodobutane (CH_3—CH_2—CHI—CH_3) the hydrogen of the methyl is more firmly joined to carbon than that in the methylene group, owing to the direct union of the latter with the second methyl.[1] Moreover, with the formation of 2-butene, the maximum entropy of the reaction is at once realized, as that hydrocarbon has a greater heat of formation than 1-butene, owing to the more intimate influences of the hydrogen atoms on the negative nucleus (CH:CH). However, from the theoretical standpoint, some 1-butene should be formed and our experiments, though not conclusive, indicate that this is the case. From similar reasons, dehydration of ethyldimethylcarbinol, or treatment of the corresponding iodide with alkali, should give chiefly trimethylethylene; still some unsymmetrical methylethylethylene should be formed, and Wagner[2] has shown that this is the case (7 per cent) with the product from the iodide.

No method of determining with any degree of accuracy the composition of a mixture of butenes has yet been described. Scheschukow[3] attempted such a determination of the iso and pseudo compounds, based on the supposition that of the two addition products formed with hydriodic acid the tertiary (from isobutene) is decomposed completely, the secondary not at all, by boiling water. Ipatiew and Ogonowsky[4] used the same methods with the bromides, but Ipatiew[5] more recently has shown that under these conditions pseudobutyl iodide is hydrolyzed to a considerable extent, and it is therefore doubtful if the bromide method can give even approximately accurate results. Konowoloff[6] liquefied the mixture of gases and absorbed the isobutene by sulphuric acid mixed with an equal weight of water. But Butlerow's statement[7] that under these conditions the pseudobutene is slowly absorbed indicates that this method cannot be accurate.

[1] Michael: J. prakt. Chem., N. F., **60**, 353.
[2] Ber. d. chem. Ges., **21**, 1235.
[3] *Ibid.*, **19**, R. 544.
[4] *Ibid.*, **36**, 1988 (1903).
[5] *Ibid.*, **40**, 1829 (1907).
[6] *Ibid.*, **13**, 2395 (1882).
[7] *Ibid.*, **9**, 77 (1878).

As the ratio of the isomeric butenes formed in different reactions is of interest in connection with the principle of partition, it would be of value to have a method of analyzing these mixtures, and we have partially succeeded in attaining this object by a modification of the methods previously used. The absorption apparatus described by Butlerow,[1] consisting of a glass tower filled with glass beads over which sulphuric acid trickles, was first tried but could not be made to give good results. The method found to be most satisfactory consisted in the use of Hempel gas pipettes with sulphuric acid of proper concentration. A sharp separation is not possible since acid sufficiently strong to dissolve one of the isomers at a rate great enough to be of service acts appreciably on at least one of the others, but such a concentration can be chosen that results correct to within a few per cent can be obtained. For use in the separation of isobutene from 2-butene, three parts of acid, by weight, are diluted with two parts of water. To analyze a mixture of 1- and 2-butenes, seven parts of acid are diluted with two parts of water, but the results here are much less accurate than in the first case.

EXPERIMENTAL PART.

Preparation of the Butenes.

Isobutene.—This was prepared by the method of Butlerow,[2] from isobutyl iodide, alcoholic potassium hydroxide, and an excess of solid alkali. The yield was 75–80 per cent. The iodide was prepared from the alcohol by means of the red, as well as the yellow, phosphorus, and iodine. The former method gave a slightly larger yield, the latter a purer product. Hydriodic acid and the alcohol give a still purer product, but the yield calculated from the amount of iodine used, is not so good.

2-Butene.—This was prepared like isobutene.[3] Eighteen grams of iodide, 36 grams of alcoholic potassium hydroxide (3 parts alcohol to 1 part hydroxide), and 15 grams solid hydroxide gave two liters of gas, *i. e.*, 87 per cent of the calcu-

[1] Z. Chem., **13**, 238 (1870).
[2] *Ibid.*, **13**, 238 and 544 (1870); Ber. d. chem. Ges., **3**, 622 (1871).
[3] De Luynes: Ann. Chem. (Liebig), **132**, 275 (1864).

lated amount. Secondary butyl alcohol was prepared according to the directions of Sabatier,[1] by passing a mixture of methylethyl ketone and hydrogen over reduced nickel. From the product the alcohol is easily obtained pure by fractionation.

1-Butene.—This was prepared like the other isomers. The yield was poor (only 24 per cent), due, as Lieben and Rossi[2] showed, in large part, to the formation of ethylbutyl ether. In the hope of improving the method by the use of a different solvent, some preliminary experiments were made on the action of alkali on ethyl iodide in acetone, glycerol, and isobutyl alcohol. Lieben and Rossi[3] state that when ethyl iodide is heated with alcoholic potash only a slight amount of ethylene is formed. We obtained ethylene in considerable quantity only when isobutyl alcohol was used.

Seven grams ethyl iodide, 15 grams isobutyl alcohol containing 15 per cent of water, and an excess of solid alkali gave over 100 cc. of gas burning like ethylene. In a second experiment, 10 grams ethyl iodide, 22.5 grams isobutyl alcohol (85 per cent), and 30 grams hydroxide gave 115 cc. gas, which burned as above and was absorbed by bromine with the exception of a few small bubbles. The yield in this experiment was only 8 per cent, but as it was an improvement over Lieben and Rossi's results with ethyl alcohol, we tried the same method with *n*-butyl iodide. Five grams of iodide, however, gave only 75 cc. of gas, so the experiments were carried no further. The slight solubility of potassium hydroxide in the alcohol used is perhaps responsible for the poor yield.

Absorption of the Butenes by Sulphuric Acid.

The apparatus described by Butlerow,[4] consisting of a glass tube 40–50 cm. long and 1.5 cm. wide, filled with glass beads, and surrounded by a jacket through which water can be passed, was used. The acid is allowed to drop in continually at the top and is drawn off at the bottom, the gas entering

[1] Compt. rend., **124**, 616 and 1358; **137**, 301.

[2] Ann. Chem. (Liebig), **158**, 166. See also Saytzew: J. prakt. Chem., N. F., **3**, 91.

[3] *Ibid.*, p. 166.

[4] Z. Chem., **13**, 238 (1870).

through a small tube at the base of the apparatus. The water in the jacket prevents any appreciable change in the temperature of the acid. The air was driven out at the beginning and the butene at the end of each experiment by carbon dioxide, which was absorbed by being passed through a bottle of alkali between the absorption apparatus and the collecting gasometer.

This method is not exact enough to give analyses of any great value, as the rate of absorption depends to a considerable extent on the rate of passage of the gas, and it was given up in favor of the Hempel pipettes. These experiments show, nevertheless, the difference in the additive power of the butenes and are of some interest.

The concentrations of sulphuric acid are given in parts of strong acid, of sp. gr. 1.8415 at 15° (97.7 per cent), to parts of water by weight.

	Parts H_2SO_4 to 1 part H_2O.	Temperature.		cc. gas		
		Acid.	Water.	Passed in.	Unabsorbed.	Per cent absorbed.
Isobutene	1.5	..	..	..	..	None, or at most very little
"	2	0°	15–16°	450	50	90
"	2	17°	17°	150	..	100
"	2	10°	10°	50	..	100
Pseudobutene	2	15°	11°	85	75	12
54 cc. Isobutene 54 cc. Pseudobutene	2	22°	13°	108	49–50[1]	...
Pseudobutene	3.75	18°	16°	32	20	37
"	3.75	18°	6°	50.4	32.2	36
n-Butene	3.75	17°	6°	55	37	33
Pseudobutene	4	16°	9°	43	8	81
n-Butene	4	17°	9°	55	28	49
Pseudobutene	5	20°	6°	66	5	91
n-Butene	3.5	18°	7°	41	41	none
"	3.5	18°	7°	20	20	none

In the above experiments the butenes were collected directly in the gasometers and, as it is impossible to prevent

[1] This series agrees well with the above experiments, which indicate that all of the iso- and a little of the pseudobutene should be absorbed. The dilution of the isobutene, however, probably prevents its complete absorption.

some air from getting in under such conditions, in the following experiments the gas was, in every case, liquefied by being passed through a U-tube with a bulb of about 2 cc. capacity at the bend, immersed in ice and salt. The sides of the tube were narrow so that when the bulb was full of liquid only a fraction of a cubic centimeter of air would be contained in the apparatus. The tube was removed from the freezing mixture and the gas collected in small glass gasometers over water that had been boiled. The mouths of the gasometers were kept constantly under water except when gas was being transferred to the burettes.

Hempel pipettes were used for these experiments,[1] and acids of a number of concentrations were employed. A mixture of 1.5 parts strong sulphuric acid to 1 part of water proved to be the best for comparison of iso- and pseudobutenes. The readings were made by transferring the gases to burettes.

Isobutene, 1.5 parts strong acid : 1 part water. Temp. 28°–29°.

A. Time. Minutes.	*B.* Reading cc.	*C.* Time interval. Minutes.	*D.* Decrease. cc.	*E.* Per cent absorbed.
0	68.2	0	0.0	0
10	21.2	10	47.0	69
20	7.6	10	13.6	89
40	1.9	20	5.9	97
160	1.6	120	0.3	98

The residue of 1.6 cc. burned with a yellow flame. In a second experiment, continued for eight hours, the residual gas would not burn, so that it is uncertain whether any other gas than isobutene was present. In any case it is impossible at present to state whether all of the slowing down in the rate of absorption is due to the presence of air or of some gas slowly absorbed.

[1] They are not the best apparatus possible since the area of the surface of the liquid, and consequently the rate of absorption of the gas, varies with the volume of the latter present. For comparative experiments, however, approximately equal quantities of the gases were used.

Pseudobutene, 1.5 parts strong acid : 1 part water. Temp. 28°–29°.

A. Time. Minutes.	*B.* Reading cc.	*C.* Time interval. Minutes.	*D.* Decrease. cc.	*E.* Per cent absorbed.
0	63.4	0	0.0	0
10	62.7	10	0.7	1
20	62.4	10	0.3	2
40	62.2	20	0.2	2
150	60.5	110	1.7	5
175	58.4	25	2.1	8
Transferred to pipette containing *5 parts strong acid : 1 part water.*				
177.5	12.8	2.5	45.6	80
182	6.7	4.5	6.1	90
194	4.6	12	2.1	93
300	3.4	106	1.2	95

Thus the pseudobutene is readily dissolved by strong sulphuric acid.

Mixture of 53.5 cc. Isobutene and 39.5 cc. Pseudobutene, 1.5 parts strong acid: 1 part water. Temp. 28°–29°.

A.	*B.*	*C.*	*D.*	*E.*
0	92.5	0	0.0	0
15	68.4	15	24.1	26
30	57.2	15	11.2	38
45	45.2	15	12.0	51
60	41.0	15	4.2	56
135	39.4	75	1.6	57
195	38.6	60	0.8	58

It is evident that when the rate of absorption has decreased to about that of the pseudobutene, the amount of gas remaining is nearly that of the above gas taken. The rate of absorption of isobutene is decreased about one-half by the presence of the other gases—approximately in proportion to the dilution. The following table, compared with the first one above, shows that the effect of change of temperature on the rate of absorption of isobutene is considerable, and other experiments might be given showing the same decrease.

Isobutene, 1.5 parts strong acid : 1 part water. Temp. 21°–22°.

A. Time. Minutes.	*B.* Reading cc.	*C.* Time interval. Minutes.	*D.* Decrease. cc.	*E.* Per cent absorbed.
0	69.2	0	0.0	0
20	29.5	20	39.7	57
40	10.2	20	19.3	85
60	4.0	20	6.2	94
120	3.3	60	0.7	95
375	2.7	255	0.6	96

This residue, on transference to a pipette containing 5 : 1 acid, was hardly affected. It will be noticed that only 39.7 cc. were absorbed in 10 minutes. A second experiment with the mixture was made.

Mixture of 37.3 cc. Isobutene and 35.0 cc. Pseudobutene, 1.5 parts strong acid : 1 part water. Temp. 21°–22°.

A.	*B.*	*C.*	*D.*	*E.*
0	72.3	0	0.0	0
20	57.2	20	15.1	21
60	42.2	40	15.0	42
100	36.6	40	5.6	49
120	35.8	20	0.8	50

The residue here is nearly equal to the amount of pseudobutene taken.

The difference in additive power of the normal and pseudobutenes is very much less than between these and isobutene, and is not great enough to permit of even an approximately quantitative separation. The following tables show the relative ease of absorption of the two gases:

Pseudobutene, 3.5 parts strong acid : 1 part water. Temp 29°–30°.

A.	*B.*	*C.*	*D.*	*E.*
0	43.7	0	0.0	0
20	35.8	20	7.9	18
40	29.4	20	6.4	33
60	24.3	20	5.1	44
80	19.5	20	4.8	55

n-Butene, 3.5 parts strong acid : 1 part water. Temp. 28°–29°.

A. Time. Minutes.	*B.* Reading cc.	*C.* Time interval. Minutes.	*D.* Decrease. cc.	*E.* Per cent. absorbed.
0	42.9	0	0.0	0
20	39.2	20	3.7	9
40	35.4	20	3.8	17
60	31.1	20	4.3	27
80	27.7	20	3.4	35

The pseudobutene is here absorbed almost twice as fast as the normal butene.[1]

Dehydration of Isobutyl Alcohol.

Various methods have been used for dehydrating isobutyl alcohol by means of sulphuric acid, with and without use of a catalyzer.

Erdmann[2] heats it with acid diluted with a small amount of water. In accordance with his directions 100 cc. alcohol, 44 cc. acid, and 16 cc. water were heated with a reverse condenser. About 4 liters of gas were obtained, 32 liters being the calculated quantity. Distillation of the residual liquid with steam gave 10–12 grams polymerized products boiling between 104° and 200°. In order to free the gaseous product from isobutene it was passed through aqueous hydrochloric acid which was kept saturated at —20° by a continuous current of gas. No tertiary butyl chloride was noticeable, but since it boils at 51° a small amount might have been formed and carried off. The amount of unabsorbed gas showed that, if present, isobutene could have been formed only in small amount. On passing the unabsorbed gas through bromine some was absorbed, and an oil boiling from 148° to 170° was obtained, which would indicate the presence of normal and pseudobutene in the original product.

[1] These experiments were carried out successively in the same pipette. In another series of experiments two pipettes with bulbs of somewhat different size were used. After a few measurements, the pipettes were changed and more readings taken. The diameter of the surface of the liquid in the two bulbs was measured roughly and a corresponding correction made in the figures for the absorption. The ratio was found to be in one case 1.8 : 1, in the other 1.6 : 1, the pseudobutene being absorbed faster. The true ratio is probably somewhere between these values and the value 2 : 1 found above.

[2] Erdmann-Bender: Chemische Präparate, II., 99.

Konowoloff[1] used 200 grams alcohol, 200 grams acid, 50 grams water, and 10 grams talc, which gave 30 liters gas, two-thirds of which, he states, was isobutene, as determined by the action of sulphuric acid diluted with an equal weight of water on the liquefied gases. In an experiment with 50 grams alcohol we obtained 6.66 liters gas, nearly the amount demanded by Konowoloff's statement. Distillation of the residual liquid with steam gave 17 grams of polymerized product, boiling at 104°–178°, with a higher boiling residue. In another experiment, with 100 grams of alcohol, 43 grams of this product were obtained.

Three hundred and fifty-six cc. of this gas were passed through two tubes of bromine cooled in ice, and, as only 24 cc. went through unabsorbed, 93 per cent of the product consisted of butenes. In a second experiment, with 250 cc. of gas, only 10 cc. went through, *i. e.*, 96 per cent was absorbed. The rate of absorption of this gas by sulphuric acid diluted with one-half its weight of water was measured, in a Hempel pipette and the mixture was thus found to contain about 60 per cent of isobutene. On treatment of the residue with acid diluted with one-fifth its weight of water, 18 per cent of the original amount remained unabsorbed after 24 hours. The original gas must, therefore, have contained, beside the butenes, a small amount of a saturated hydrocarbon, and also some of an unsaturated one which is not identical with any of the butenes.

According to Ipatiew,[1] when isobutyl alcohol is passed through a copper tube filled with zinc chloride and heated to about 500° a mixture containing all the butenes is formed, but when a copper or glass tube containing fragments of a graphite crucible or of aluminium oxide is used, only isobutene is obtained. This appeared to be the best method for preparing isobutene, but on repeating the experiments of Ipatiew we were not able to obtain the same results.

In our first experiment we used a Jena combustion tube,

[1] Ber. d. chem. Ges., **13**, 2395.
[2] *Ibid.*, **36**, 1990.

which was filled with pieces of a graphite crucible[1] that had previously been ignited in a covered Hessian crucible. The tube was heated in a L. Meyer[2] furnace for heating tubes; we found no difficulty in keeping the temperature of the tube fairly constant at 500°. Sixty-five grams of alcohol gave 29 liters of gas, but a large part of it was not isobutene. It could not be liquefied by passing through a tube cooled in ice and salt to —18°, nor was any alkyl chloride obtained by passing it through aqueous hydrochloric acid saturated at the same temperature, although isobutene unites readily with the acid under these conditions.[3] Five liters were then passed twice through bromine and only 1.75 liters were absorbed; in a second experiment with 6.5 liters, 2.5 liters were absorbed. The boiling point of the product thus obtained indicated the presence of more iso- than pseudobutylene bromide with, possibly, a little of the normal derivative. A second lot of gas was then prepared. Three liters were passed twice through hydrochloric acid at —18°, and nearly one liter was absorbed. Of the residue, 0.4 liter was absorbed by bromine, the oil formed boiling at 148°–164°—mostly near 155°, the boiling point of the pseudo compound. If only isobutene was absorbed by the hydrochloric acid, the ratio of iso- to pseudobutene would thus be 2.3 : 1.

Aluminium oxide (Kahlbaum's C. P.) was then used as the catalytic agent. Eight and one-tenth liters of the gas were passed through bromine cooled in ice, and 4.5 liters were absorbed. A considerable amount of dibromide, boiling from 145° to 165°, was then prepared and fractionated. Only a partial separation was possible, but the results indicated that approximately two-thirds of the product was iso-, one-third pseudobutylene bromide, with a comparatively small amount which might have been the normal bromide. The residue unabsorbed in bromine burned with a slightly luminous flame, but not much carbon dioxide was produced by the combustion.

[1] The crucible had been previously employed for another purpose, but the pieces used were as far as possible freed from foreign substance.

[2] Ber. d. chem. Ges., **16**, 1087.

[3] Le Bel: Bull. Soc. Chim., **28**, 460.

The temperature in the above experiment was measured by means of a mercury thermometer filled with carbon dioxide. After the last experiment the bulb was found to be enlarged, so that the temperature may have been considerably above 500°. A thermocouple was then used and the experiments repeated. With pieces of a new graphite crucible, 30 grams of alcohol gave 8 liters of gas in 50 minutes; with aluminium oxide the same amount of alcohol gave 6 liters in 65 minutes. The gases so obtained were analyzed by means of sulphuric acid in the Hempel pipettes.

Gas obtained with Graphite Crucible, 1.5 parts strong acid: 1 part water. Temp. 15°.

A. Time. Minutes.	*B.* Reading. cc.	*C.* Time interval. Minutes.	*D.* Decrease. cc.	*E.* Per cent absorbed.
0	100.5	0	0.0	0.0
40	73.6	40	26.9	26.9
70	59.3	30	14.3	41.2
120	48.2	50	11.1	52.3
150	46.2	30	2.0	54.3
210	44.6	60	1.6	55.9
405	42.3	195	2.3	58.2

Beginning with the sixth reading the isobutene may be considered as completely absorbed.

Same Gas as above, 5 parts strong acid: 1 part water.

A.	*B.*	*C.*	*D.*	*E.*
0	100	0	0.0	0.0
3	36.4	3	63.6	63.6
6	21.0	3	15.4	79.0
10	9.6	4	11.4	91.4
55	3.8	45	5.8	96.2
125	3.7	70	0.1	96.3

There thus appears to be about 55 per cent of isobutene, with about 2.5–3.0 per cent of gas not a butene at all. The latter result was confirmed by passing 0.90 liter of the gas through two tubes of bromine, when 20 cc. (2.2 per cent) were unabsorbed.

With the gas from aluminium oxide nearly the same results

were obtained, but the amount of isobutene was somewhat greater (65–70 per cent), and about 5 per cent was unabsorbed by 5 : 1 sulphuric acid. Some of the gas was passed through bromine cooled in ice and the unabsorbed gas analyzed by combustion. Thirteen and eight-tenths cc., mixed with 45·3 cc. of air, were exploded and underwent a contraction of 5·3 cc., no carbon dioxide being formed. If all had been hydrogen the contraction should have been 20·7 cc., while if there had been any hydrocarbon present some carbon dioxide should have been formed. It thus appears that there was approximately 1 per cent of hydrogen present in the original product, with about 3–4 per cent of air.

It appears from these experiments that slight differences in the catalytic agent may have considerable effect on the nature of the product obtained by the Ipatiew method and that the conditions necessary for the preparation of pure isobutene from isobutyl alcohol are not at present sufficiently well defined.

Preparation of the Higher Alkenes.

The amylene used was Kahlbaum's trimethylethylene, which is probably prepared[1] by dehydrating tertiary amyl alcohol with oxalic acid. The Kahlbaum product was boiled with sodium until the sodium remained unaltered, and then distilled through a column of beads. The whole product boiled at 37°–38°.

The only hexylene investigated was tetramethylethylene. This alkene was made by Couturier[2] from pinacone dibromide, and was considered pure until Kondakow[3] showed that it is a mixture. More recently Delacre[4] prepared a pure product, starting from dimethylisopropylcarbinol. This compound was prepared by the action of magnesium-methyl iodide on the ethyl ester of isobutyric acid. Delacre[5] found that the product obtained in this way was identical with that obtained from magnesium-isopropyl bromide and

[1] Z. angew. Chem., **93**, 202.
[2] Ann. chim. phys. [6], **26**, 461.
[3] J. prakt. Chem., N. F., **59**, 293.
[4] Centralb., **1906**, II., 498.
[5] *Ibid.*, p. 1719.

acetone, and that both gave bromides identical with that formed by addition of hydrobromic acid to tetramethylethylene. The yield of tertiary hexyl alcohol obtained from isobutyric ester was very poor. Twelve grams ester gave 7.5 grams product boiling at 117°–119°; and in another experiment 68 grams ester gave 21 grams product boiling at 118°–119°.5, or about 27 per cent of the calculated yield. The iodide was obtained by saturating with hydriodic acid gas and allowing the mixture to stand overnight, extracting with sodium carbonate, and then with water. After drying with phosphorus pentoxide and distilling in vacuum with beads, the product boiled constantly at 52° (23 mm.), and the yield was nearly quantitative. Tetramethylethylene was prepared from the iodide by means of alcoholic potash with excess of solid hydroxide in the proportions used with isobutyl iodide, the hydrocarbon being separated by addition of water to the mixture; also by treatment with 10 per cent aqueous potash, the amount used being the same as in the first case. The yield by the second method was somewhat better, but prolonged boiling, with frequent shaking of the mixture, was necessary to decompose all of the iodide. The tertiary carbinol formed and any ethyl alcohol present were removed by treatment with a small amount of phosphorus pentoxide. Fifty grams iodide gave 7.5 grams of product boiling at 71°–72°.5.

Diisobutylene was prepared according to Butlerow's[1] directions, by dissolving liquid isobutene in dilute sulphuric acid and heating to 100°. After 4–5 hours' heating there is little, if any, increase in the amount of polymerized product; indeed, the reaction is practically complete in a much shorter time. In one experiment sulphuric acid of sp. gr. 1.842 (= 97 per cent H_2SO_4) diluted with an equal volume of water was used. In this case nearly half of the product consisted of triisobutylene and high-boiling products, while, when the acid was diluted with an equal weight of water (Butlerow's proportions) about 80 per cent of the product was the dipolymerized derivative, which was easily purified. The total yield of polymerized product was 80–90 per cent

[1] Ann. Chem. (Liebig), **189**, 48 (1879).

of the isobutene used, 60 per cent of which distilled at 102°–102°.5 after being boiled with sodium, while a small amount of triisobutylene, boiling point 176°–178°, was obtained.

The hydrocarbons obtained from the mother liquors in the preparation of isobutene by the methods of Konowoloff and Erdmann[1] were dried and fractionated, but no sharp-boiling fractions could be obtained, even after repeated fractionation, the liquids distilling from 102° to over 260°.

Triisobutylene was prepared by passing isobutene slowly into sulphuric acid diluted with one-fifth its weight of water, and kept at about 4°, and allowing the mixture to stand overnight at room temperature. The oil which separated represented a yield of 60–70 per cent, but was not pure triisobutylene, as it boiled from 160° to higher than 200°. We varied the method by heating the solution to 100° as soon as the isobutene had all been passed in, also by using acid diluted with one-third its weight of water and working in the cold, but judging from boiling point the product was not improved in either case.

ADDITIVE POWER OF THE HYDROCARBONS.

Isobutene and Trimethylethylene.

Sulphuric Acid of Sp. Gr. 1.842 Diluted with One-half its Weight of Water.—Two tubes, each containing 2 cc. of acid, and one about 0.3 cc. liquefied isobutene, the other an equal volume of trimethylethylene, were cooled in ice water, then kept at this temperature and shaken. The butene dissolved in 4 minutes, the amylene in 12 minutes; after 1–2 hours the solutions became turbid, owing to the formation of polymerization products.

Sulphuric Acid with an Equal Weight of Water.—Four tubes, each with 2 cc. acid, one set of two with isobutene, the others with amylene, kept cold and shaken for 18–20 minutes. The butene had dissolved, but the volume of the amylene had only slightly decreased. The amylene tubes were then put in the shaker at room temperature. It required nearly two hours before solution was effected.

[1] See above.

Sulphuric Acid with Twice its Weight of Water.—A small amount of amylene stood more than 40 hours, part of the time in a shaking machine, before dissolving, while a larger amount of isobutene gave a clear solution in 12 hours with only occasional shaking.

Phosphoric acid was made up to 0.5 normal. Two tubes containing 1.5 cc. acid and 0.2 cc. amylene, and two others with the same amount of acid and as nearly as possible the same amount of isobutene, were shaken about 9 hours a day. After 55 days the butene was dissolved while the amylene was scarcely affected.

With *hydrochloric acid* (0.577 *N*) similar experiments were carried out with the result that the butene was dissolved in ten days, except a trace of yellow oil which did not disappear after 30 days longer and was probably polymerized product, while the amylene required 40 days.

It appears from these experiments that isobutene is dissolved by the acids used at least three times as fast as trimethylethylene.

Trimethylethylene and Tetramethylethylene.

Three Parts Sulphuric Acid with Two Parts Water.—Four tubes, each containing 0.360 gram acid, two with 0.030 gram of the amylene, and two with 0.036 gram of the hexene, the molecular proportion of hydrocarbon to acid being in each case 1:5, were kept in ice water, but shaken frequently. After 1.25 hours the amylene had dissolved (the solution on standing overnight began to polymerize), while the hexene was not noticeably changed.

Sulphuric Acid with One-half its Weight of Water.—Tubes with acid and hydrocarbon in the same molecular proportion as above. The amylene dissolved in 35 minutes, while the hexene did not change in 6 hours, although on standing overnight nearly all of it went into solution. Polymerization takes place faster in the amylene than in the hexene solutions, having already begun with the former after 24 hours in the above experiment. After a week, however, a layer of oil of nearly the same thickness as the original one

had appeared in the hexene tubes. After 15 days these were opened, the oil was dried with a little phosphorus pentoxide, and distilled. The boiling point was considerably above 100°, which is sufficient to show that polymerization had occurred.

With *sulphuric acid diluted with one-fourth its weight of water*, the tubes lying on their sides in ice water, the hexene was found to dissolve in 20 minutes and to begin to polymerize in 2.5 hours.

With *hydrobromic acid*, similar results were obtained. An aqueous solution of 4.56 N acid dissolved the amylene in 4 hours but showed no noticeable action on the hexene in 56 days. With 2 N acid the amylene dissolved in 0.75 hour but the hexene little, if at all, in 50 days. It was also found, both by titration of the acid and by the boiling point of the oily layer, that the hexene had not formed any hexyl bromide.

The difference between the tri- and the tetramethylethylene is thus much greater than between the first compound and isobutene. In the former case the ratio is at least 12 : 1, when 2 : 1 sulphuric acid is used.

Tetramethylethylene and Diisobutylene.

The hexene having been found to dissolve in 4 : 1 sulphuric acid in a few minutes, diisobutylene was tried with the same acid. This did not dissolve at all, judging from the thickness of the oily layer, but after 12 days' standing, most of the oil was found to boil above 140°, although some of the original substance (boiling point 102°–103°) was still present.

With *8.06 N hydrobromic acid* four tubes were prepared and shaken about 9 hours a day. Two containing the hexene were opened after 50 days, two with the octene after 65 days. In the former, 80 per cent of the hydrocarbon had formed bromide, while the presence of a tertiary carbinol was ascertained by diluting the solution, distilling, and salting out the distillate. The boiling point of the oil in the tubes —120°–140°—indicated that none of the original hydrocarbon (boiling point 72°) was left. In the octene tubes 32 per cent of the hydrocarbons had been converted into bromide. The

oil distilled mostly at 102°–105°, although there was a little of the higher boiling products. This result shows that considerable diisobutylene (boiling point 102°–103°) was still unchanged.

AN ELECTRICALLY-CONTROLLED GAS REGULATOR.

By E. Emmet Reid.

In some work which is being carried on at various fixed temperatures and where accurate and reliable gas regulation is required, the following regulator has proved entirely satisfactory.

A glass U-tube of about 8 mm. internal diameter (T T T, Fig. 1) is provided with a side tube V and is enlarged at the top for the reception of a small rubber stopper, S S. Through this stopper passes a tube, N O, with an external diameter 1 mm. less than the internal diameter of the U-tube. The U-tube is filled with mercury, H H H, to the level L L, a millimeter or so below the end of the tube N. The weight W is a piece of iron about 7 mm. in diameter and 15 to 20 mm. long. This is suspended freely from a hook, C, on the armature of an electro-magnet, M M. The armature is held up by a spring which is fastened rigidly to the block B. The spring is adjusted to support the weight but to yield quickly to the magnet. The length of the wire C must be such that its end will have a vertical motion of 1 or 2 mm. Greater motion than this is not required but will do no harm. The iron rod W must be suspended flexibly and freely rather than rigidly so that it acts simply by its own weight on the mercury. If the sudden motion of the armature be rigidly and suddenly transmitted to the mercury, the latter may splash into the side tube V.

The gas enters at N and, normally, flows under the lower end of this tube up through the annular space E and out to the burner through the side tube V. When the electro-magnet is actuated the lowering of the weight W causes a corresponding elevation of the mercury at O and cuts off the gas. A pin hole at P allows enough gas to pass through to

keep the burner lit. In constructing the apparatus two or three very small pin holes may be made and closed with paraffine. One or more of these, as the size of the burner or stove may require, can be opened with a hot needle to allow the

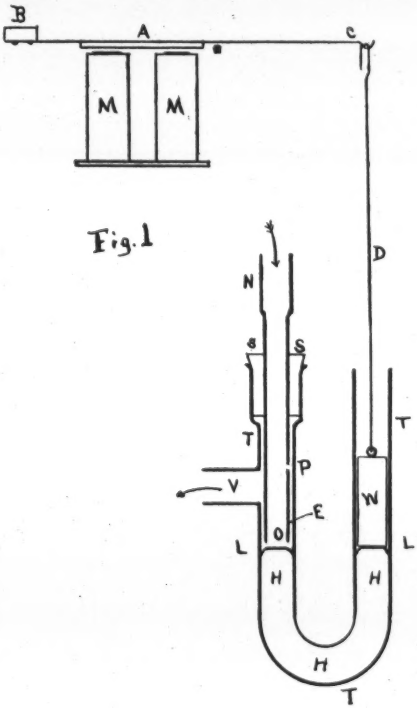


Fig. 1

passage of gas for a pilot flame, or the burner may be provided with an independent supply of gas to keep it lit. The surface tension of mercury is so great that though the weight W fits only loosely in the tube the mercury will not enter the annular

space around it. Thus W acts as well as an air-tight piston. On the other side the pressure of the gas is not sufficient to drive the mercury into the annular space there. To get the full advantage of this fact the gas should be made to enter through the central tube N and go out at V, and not the reverse.

As a motion of only 1 or 2 mm. is required for the weight W, and as this weighs only about 7 grams, the work required of the electro-magnet is very slight.

For the electro-magnet an ordinary electric bell of the cheapest form may be used, the vibratory make-and-break being short-circuited and the bell removed. The connection D may then be hung on the end of the clapper. The magnet may be wound up to 20 ohms to economize current. With this resistance in the electro-magnet, a single storage cell will give excellent service, while with less resistance, an ordinary dry cell is all that is required.

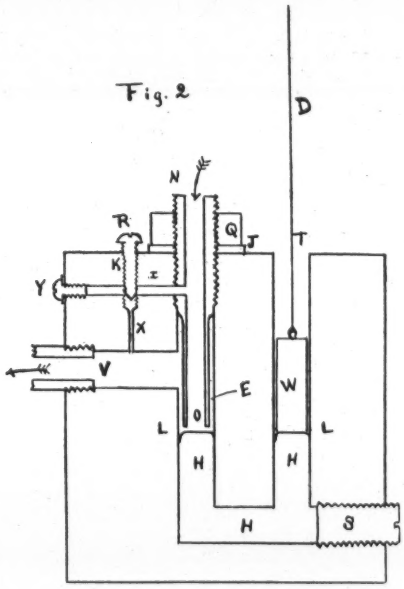
Instead of being suspended, W may be floated on the mercury, the amount of which is so adjusted that the gas can pass properly. In this case, instead of using the electro-magnet, a coil of wire of suitable size and length is wound around the limb of the U-tube containing W. The resistance of the coil should be from 5 to 20 ohms, according to the battery used. This coil is placed somewhat below the center of W. When the current is passed through this solenoid, W is drawn down and the gas cut off as before. W should be made of the softest iron obtainable. This plan requires more current but is simpler.

The apparatus can be controlled by any of the forms of electrical regulators on the market, in which a contact is made when a certain temperature is exceeded and broken when the temperature goes down. As these regulators may be made of extreme sensitiveness the regulation of temperature to any required degree of accuracy may be accomplished.

The advantage of this form of regulator is that it can be made quickly and easily out of materials at hand in the chemical laboratory. It may be readily cleaned. The large gas opening permits of much fouling of the mercury before cleaning is required.

In Fig. 2 is shown another regulator based on the same principle. It is made of a block of cast iron, about 2 x 2 x ¾ inches or 60 x 60 x 18 mm., into which holes are drilled. As most of these correspond to the tubes in the other figure and are lettered in the same way they will not be redescribed. The main holes may be of the same size as the tubes in Fig. 1,

Fig. 2



or may be of any size suitable for the supply of gas required. S is a plug which may be used to regulate the height of the mercury in the U-tube. Should the mercury become foul it may be removed by taking out S, cleaned, and replaced. The inlet tube N O is made in the shape shown, its lower part being turned down on the lathe so as to leave the proper space

for the gas. Its upper portion is threaded with straight thread so as to screw into the block. When it is put in place the lock-nut Q is screwed on firmly over the lead washer J. Then the hole I is drilled through the block and into the tube N. The outer end of this hole is closed by the screw plug Y which is provided with a lead washer. The hole K is drilled so as to intersect I, and is continued by the small hole X which opens into the outlet V. A pointed screw, R, serves as a needle valve to regulate the by-pass and supply any amount of gas desired to keep the burner or stove lit.

A gas-pipe thread may be cut on the extreme upper end of N and the supply pipe screwed on directly. The hole V is tapped to receive the iron gas pipe for the burner. The advantage of this form over the other is that, being entirely of metal, it is unbreakable and compact, and eliminates any danger of fire. The operation is the same as that of the other form.

The work of which this is a part is being carried on by the aid of a grant to Prof. S. F. Acree, by the Carnegie Institution.

JOHNS HOPKINS UNIVERSITY, BALTIMORE, MD.,
January 5, 1909.

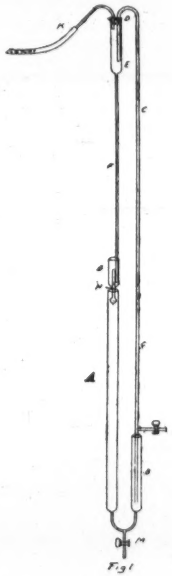
AN APPARATUS FOR THE PURIFICATION OF MERCURY.

BY L. JUNIUS DESHA.

The purification of mercury has often been accomplished in the laboratory by pouring the metal from a funnel with a minute capillary outlet through a column of dilute nitric acid (or other cleansing solution) about one and one-half meters in height. When repeated sufficiently often, this process is very effective. But the frequent attention necessary for returning the mercury from the lower receiver to the funnel seriously interferes with other work during the long time required for satisfactory purification, and there is therefore always a natural tendency to stop the operation too soon. Having to purify a considerable quantity of mercury *very thoroughly* I cast about for some means of avoiding this waste

of time. Professor S. F. Acree suggested to me the automatic principle of the apparatus now to be described and I am further indebted to him for assistance in working out some of the details.

A and B (Fig. 1) are tubes 22 mm. in diameter and 90 and 35 cm., respectively, in length, connected by fusion of their lower ends to the small curved tube which bears the glass



stop-cock M. C is made of thick-walled glass tubing 1.5 mm. in bore and about 200 cm. in length, to which a side tube with glass stop-cock, L, is fused just above B. Its lower end hangs loosely in B near the constriction and the upper end passes through the rubber stopper D into the tube E. The latter is 20 mm. wide and 150 mm. long, terminating in the

thick-walled capillary F (76 cm. long) which extends to the bottom of the mercury trap G. The capillary tube H is fused into G; its upper end is expanded and extends 25 mm. above the outlet of F while its lower end, extending 10 cm. into the liquid in A, is blown into a small bulb containing several very small holes. A second tube leads from E through D to the suction pump.

Mercury is poured into A or B in any desired quantity (provided only that it extends above the lower end of C) and then the remainder of A is filled with the purifying agent, which is usually one per cent nitric acid. The trap G having been filled with mercury to the level of the top of H, the suction pump is turned on. Under the diminished pressure thus produced in C and E, mercury is drawn from B into C, the stop-cock L being so adjusted that alternate small portions of mercury and air are drawn up into E.[1] At the same time mercury is, of course, drawn into F from G until a pressure is attained which balances that in C. The mercury drawn through C into E runs down through F into G, then over the top of, and into, H and is discharged into the cleansing solution in A through the minute openings in the bulb of H.

Such an apparatus has been in use here now for several weeks and the results have been most satisfactory. The advantages which it offers may be summarized as follows. The process is perfectly continuous for a given lot of mercury and requires absolutely no attention after once being started. The apparatus may be used equally well for large or small quantities of mercury. By suitable and easy adjustment of the stop-cock L, the maximum efficiency for any given pump may be readily attained. The cleansing solution, when exhausted, may be siphoned off and replaced by a fresh one; pure mercury may be withdrawn at M. As the apparatus consists only of glass (with the exception of the rubber stopper D which does not come into contact with the mercury) there is no chance for the introduction of impurities, and the individual parts may readily be removed and cleaned when

[1] Dr. B. B. Turner has called my attention to a similar arrangement used by Boltwood in his modification of the Sprengel pump. Cf. THIS JOURNAL, **19**, 76.

necessary. When a No. 3 Chapman pump is attached to the apparatus 100 cc. of mercury are passed through the cleansing solution once in about eight minutes.

Though the very fine division of the mercury, as it passes through the nitric acid, insures large surface and therefore very thorough cleansing, I propose to still further increase the purity of the product by combining an electrolysis with the present arrangement. This can be accomplished very simply. A platinum plate will be hung in A beside the bulb of H and surrounded by a silk bag. A small platinum wire will make electrical connection with the mercury in H which will be made the anode. A small current will then be passed between it and the platinum plate in the nitric acid. The impurities in the minute charged globules leaving H should electrolyze out very easily, while the bag will prevent any deposit formed on the cathode from dropping to the main body of mercury below.

THE JOHNS HOPKINS UNIVERSITY,
December 24, 1908.

REPORTS.

HYDROGEN PERSULPHIDES.[1]

Persulphides of hydrogen were discovered by Scheele in 1777; since then many prominent chemists have studied these substances and have devised new methods for their preparation. We find references in text-books to compounds of the compositions H_2S_2, H_2S_3, H_2S_4, H_2S_5, but no one has hitherto succeeded in obtaining any one of these substances in pure condition.

As raw material Bloch used crude sodium polysulphide, which he made by heating crystallized sodium sulphide ($Na_2S + 9H_2O$) with a weighed amount of sulphur on the water bath; the sodium sulphide melts in its water of crystallization, dissolving the sulphur. The product, which is dissolved in water, approaches the compositions Na_2S_2, Na_2S_3, Na_2S_4, or Na_2S_5 according to the proportion of sulphur used. The solution is put in a dropping funnel under hydrogen pressure and is run slowly into a large beaker containing hydro-

[1] Abstract of four articles by Ignaz Bloch and pupils in Ber. d. chem. Ges., **41**, 1961 (1908).

chloric acid and ice, which is kept at a temperature of —10° by means of a freezing mixture. The contents of the beaker are constantly stirred. An emulsion is thus obtained which deposits a yellow oil. This oil is dried by calcium chloride which has been previously treated with dry hydrochloric acid gas. Otherwise the calcium chloride is alkaline enough to partly decompose the hydrogen persulphide. All vessels which come into contact with these persulphides must likewise be treated with hydrochloric acid gas to neutralize the alkalinity of the glass. Indeed, Bloch ascribes the failure of previous workers, from Scheele down, to obtain pure substances to the neglect of this precaution.

By distilling 50 cc. crude polysulphide at a pressure of only 2 mm., 8 cc. distillate in three fractions were obtained. The middle fraction proved to be pure hydrogen trisulphide, H_2S_3.

Hydrogen trisulphide is at ordinary temperatures a pale yellow liquid; at low temperatures it is colorless. It has the consistency of olive oil and a specific gravity of 1.496 at 15°; it boils under 2 mm. pressure at 69°, and solidifies at —52° to —59°. Its odor is penetrating and disagreeable, recalling that of sulphur chloride and camphor, and its vapors attack the mucous membranes. It decomposes gradually on standing, more quickly in the light than in the dark, forming hydrogen sulphide and free sulphur. It is decomposed by alkalies and by alcohol. It is soluble in ether, benzene, and carbon disulphide, forming comparatively stable solutions. It dissolves sulphur at ordinary temperatures, but on the addition of benzene the dissolved sulphur is precipitated.

In the preparation of hydrogen trisulphide Bloch protected the mercury pump by means of a potash bulb between the pump and the receiver. Noticing that the potash turned yellow, he introduced a second receiver and found that while the trisulphide condensed in the first receiver as before, a more volatile liquid collected in the second. This proved to be hydrogen disulphide, H_2S_2. He also made the disulphide by distilling pure trisulphide at 100° under 20 mm. pressure. About one-third of the trisulphide changed to disulphide, one-third distilled undecomposed, and the remainder was decomposed into hydrogen sulphide and sulphur.

Hydrogen disulphide, H_2S_2, is a clear yellowish liquid at ordinary temperatures. Its specific gravity is 1.376. It is more stable than the trisulphide, as it can be distilled in great part without decomposition under atmospheric pressure at 74°–75°. It does not solidify in a mixture of ether and solid

carbon dioxide, differing in this respect from the trisulphide. In all other respects it resembles the trisulphide but is chemically more active.

The analytical data for both of these sulphides show that the substances obtained were pure. The methods used were: (*a*) determination of the amount of hydrogen sulphide liberated by the action of acid; (*b*) determination of hydrogen, by combustion with lead chromate; (*c*) determination of the total sulphur by the method of Carius. In making the sulphur analyses Bloch found that the fumes of the nitric acid, acting on the trisulphide, caused an explosion during the sealing of the tube; to prevent this he froze the nitric acid in the tube, and then added the weighed sulphide in a glass-stoppered weighing bottle, sealed the tube, and allowed the acid to thaw in a tube furnace.

With an ordinary vacuum distilling apparatus the yield of pure sulphides was variable and unsatisfactory. Bloch therefore devised an apparatus so ingenious and useful for fractional distillation that it seems well to copy his description of it and of the method of work.

The 300 cc. Anschütz flask A (Fig. I.) is connected by a long condenser with the receiver B (a 150 cc. distilling bulb), and this, in turn, with the vessel C which is cooled by a mixture of ice and salt. The flask A is also connected by the tube E to the deep U-tube F. The T-tube H leads through soda-

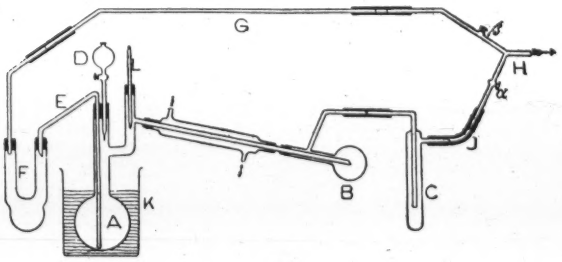


Fig. I.

lime and calcium chloride tubes and a manometer to a mercury pump. By opening or closing alternately the stopcocks α and β, the pump is connected either with the vessel C or through the tube G with the U-tube F. The flask A is filled through the dropping funnel D.

The method of procedure is as follows: After hydrochloric acid gas has been passed for 10 minutes through the whole apparatus, the glycerol bath K is heated to 110°–125°. The stopcock α is then opened and β is closed and the pressure is reduced to about 20 mm. About 15 cc. of crude hydrogen polysulphide are allowed to run slowly into the flask; in 30 seconds the liquid foams and distils evenly into the receiver B, the temperature of the vapors rising above 60°, as shown by the thermometer L. The foaming and distillation soon nearly cease almost entirely. Stopcock α is now closed and β opened, the residues in A being drawn over into F. The stopcocks are then reversed and a new distillation with another 15 cc. portion of polysulphide begun.

The distillate in A is nearly pure hydrogen trisulphide; by drawing a little air over it, traces of hydrogen sulphide and some trisulphide are removed, and by freezing it and pressing the frozen mass it is completely purified. The distillate in C is hydrogen disulphide and is purified for analysis by a single distillation at atmospheric pressure. The yield from 100 cc. crude polysulphide is from 30 to 33 cc. of trisulphide and from 10 to 15 cc. of disulphide.

The apparatus described will be found convenient for distilling any substance which cannot be distilled in larger portions without general decomposition.

Bloch proposes several constitutional formulas for the di- and trisulphides, but admits that he has not thus far enough experimental evidence to confirm any one of them.

He does not believe that hydrogen trisulphide is the last member of the series H_2S_n. As the strychnine salt of the hexasulphide, H_2S_6, has been carefully studied by A. W. Hofmann, and its brucine salt by E. Schmidt and later by Bruni and Borgo, who also made the benzyldiamine salt, while the brucine salt of the octosulphide, H_2S_8, has been made by Döbner, Bloch thinks there can be no doubt as to the existence of the hexa- and octosulphides of hydrogen.

As the disulphide, H_2S_2, is formed by heating the trisulphide H_2S_3, Bloch does not believe that the former is present in the crude polysulphide, nor does he believe that this crude polysulphide made from crude Na_2S_4–Na_2S_5 contains the trisulphide, for the following reasons: pure trisulphide dissolves in benzene in any proportion without decomposition. Sulphur dissolves freely in the trisulphide, but if benzene is added to this solution the dissolved sulphur is precipitated. If then crude hydrogen polysulphide were simply a solution of sulphur in hydrogen trisulphide, benzene should precipitate the

dissolved sulphur. As a matter of fact, the polysulphide dissolves freely in benzene, forming clear solutions. This leads Bloch to the conclusion that all of the sulphur in the crude polysulphide is chemically combined with hydrogen, that the trisulphide is formed by a breaking down of higher polysulphides contained in the crude material, and that probably some or all of these higher members of the series H_2S_n can be isolated in pure condition. E. R.

PREPARATION OF ARGON FROM AIR BY MEANS OF CALCIUM CARBIDE.

Franz Fischer and Oskar Ringe[1] have worked out a method whereby they are able to obtain argon of a high degree of purity in comparatively large quantities with simple and inexpensive apparatus.

Atmospheric air contains 0.937 per cent, by volume, of a mixture of the so-called "noble gases," which, in turn, consists of 99.75 per cent of argon and 0.25 per cent of helium, neon, krypton, and xenon. Cavendish first noticed that when air is sparked in the presence of an excess of oxygen and the oxides of nitrogen and the remaining oxygen are absorbed, about 1/120 of the original volume of air remains unabsorbed. Ramsay and Rayleigh later used this method to isolate argon; in this manner the latter was able to obtain 2 liters of this gas. Afterwards these same investigators employed magnesium to absorb the nitrogen after the oxygen had been removed by means of copper heated to redness. Maquenne suggested the use of a mixture of lime and magnesium, which react according to the equation

$$CaO + Mg = MgO + Ca,$$

the calcium then energetically absorbing the nitrogen with the formation of calcium nitride, Ca_3N_2. As calcium can now be prepared electrolytically at quite a low cost, this metal has, of late years, been used almost exclusively to absorb the nitrogen.

Fischer and Ringe have found that at 800° a mixture of 90 per cent of finely pulverized calcium carbide and 10 per cent of anhydrous calcium chloride absorbs the nitrogen in air quantitatively, forming calcium cyanamide and carbon according to the equation

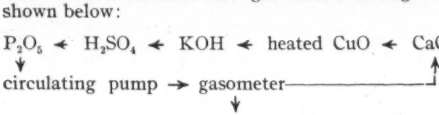
$$CaC_2 + N_2 = NC.NCa + C.$$

As the price of the carbide is low, it is used to absorb the oxygen also. The final products in this case are lime and free

[1] Ber. d. chem. Ges.; **41**, 2017 (1908).

carbon, carbon dioxide and monoxide being formed as intermediate products. The carbide thus serves to absorb everything but the noble gases and hydrogen which may be formed from traces of water present in the calcium chloride.

The absorption vessel consists of an iron box with walls 8 mm. thick, 50 cm. long, and 17 cm. wide and provided with inlet and outlet tubes of the same material and suitably cooled at the points where they emerge from the box. It is placed in a brick furnace and heated with gas burners. A vessel of these dimensions will hold 7 kilograms of carbide. After it has been exhausted and heated to remove the gases and tarry products formed by the action on the carbide of the water which is always present in the calcium chloride, it is connected with a series of tubes and gasometers arranged in the order shown below:



Dry air is now slowly admitted until the pressure in the whole apparatus is about equal to that of the atmosphere. The supply of air is then shut off, and by means of a simple mercury circulating pump, which is fully described in the authors' paper, the gases in the apparatus are drawn repeatedly over the heated copper oxide and the series of absorbents into the gasometer, and back again into the carbide vessel, etc., until there is no further diminution in pressure. Any hydrogen which may be formed or carbon monoxide which is not acted upon by the carbide is burned by the copper oxide to water and carbon dioxide, respectively, and is absorbed in the next tubes in the series. The argon is finally drawn into the reserve gasometer, a fresh supply of air admitted to the apparatus, and the process repeated until the carbide is exhausted. In this way, with 7 kilograms of the carbide mixture the authors obtained in 22½ hours 11 liters of "Rohargon," *i. e.*, a mixture of 99.75 per cent argon and 0.25 per cent of the other noble gases. Specific gravity determinations showed that there could not be more than 0.1 per cent of nitrogen in the product. C. A. R.

REVIEWS.

A TREATISE ON QUALITATIVE ANALYSIS AND PRACTICAL CHEMISTRY. Adapted for Use in the Laboratories of Colleges and Schools. By FRANK CLOWES, D.Sc., Lond., Emeritus Professor of Chemistry in the University College, Nottingham. Eighth Edition. London: J. and A. Churchill; Philadelphia: P. Blakiston's Son and Co. 1908. pp. XXIII + 518. Price, $3.00.

This volume is unlike any other of our text-books. Much of the matter is copied from the "Elementary Practical Chemistry" by Clowes and Coleman (reviewed in THIS JOURNAL[1]), but although the field is restricted to qualitative analysis, the size and scope of the book are much enlarged.

A large part of it is given to the preparation and properties of gases, and the properties of substances, both organic and inorganic. Much space is devoted to apparatus, laboratory fittings, and other matters interesting to the teacher more than to the student.

The methods are all the common well-tried ones, and do not go beyond the ordinary needs of the technical chemist. No use is made of any phase of physical chemistry.

The book can be recommended as a good manual for teachers in high schools and technical schools, and for technical chemists.

E. R.

LABORATORY MANUAL OF QUALITATIVE ANALYSIS. By WILHELM SEGERBLOM, A.B., Instructor in Chemistry at the Phillips Exeter Academy. New York, London, Bombay, and Calcutta: Longmans, Green, and Co. 1908. pp. XII + 136. Price, $1.25.

This is a good laboratory manual for beginners, clearly written and full of detail. It contains nothing original or novel.

E. R.

ELEKTROANALYTISCHE SCHNELLMETHODEN. Elektroanalyse unter Bewegung von Elektrolyt oder Elektrode. Von DR. ING. A. FISCHER, Technische Hochschule, Aachen. Mit 41 Abbildungen und 136 Tabellen. Stuttgart: Verlag von Ferdinand Enke. Preis, M. 9.40.

This book of 300 pages comprises volumes IV.-V. of "Die Chemische Analyse" by Dr. B. M. Margosches. The excellent presentation of the theory of electroanalysis, as set forth in the first 70 pages of this work, fills an important gap in the literature of analytical chemistry. Many chemists have avoided the use of electroanalysis, or have not obtained good results from these methods, because of a lack of understanding of the subject. To obtain even a working knowledge from the original literature required the expenditure of

[1] **38**, 251; **39**, 311.

a great deal of time and patience. To chemists thus situated, and to the student of the subject in general, the book will prove of great value.

The theory of the reduction and separation of metals and the bearing of polarization on the subject is ably handled from the standpoint of the well-known Nernst formula. Considerable space is devoted to the important rôle played by diffusion and complex salts, and to the influence of temperature and of stirring. More might have been profitably said, perhaps, with regard to the various factors governing the form of metallic deposits, and exception might be taken to some of the statements under this head on pages 41–42. No mention is made of Bancroft's comprehensive articles on this subject.[1] Some thirty pages, which are illustrated by numerous very excellent drawings and photographs, are devoted to the description of modern apparatus and to the sources of current.

In the practical part of the book the elements to be considered are divided according to their electrical behavior into six groups. A great deal of information about the various procedures for determining the individual metals is condensed into tabular form, and pains have been taken with the numerous references to the original literature. The author does not give his "besondere Gründe" for leaving out the work done with the mercury electrode, but the advisability of making such an omission is open to question.

In the last part of the book a number of practical determinations, such as the rapid analysis of brass and bronze, are given. Most of these have been carried out in the author's own laboratory. To any one interested in electroanalysis this book is highly recommended. E. B. SPEAR.

DETERMINATION OF RADICLES IN CARBON COMPOUNDS. By DR. H. MEYER, Professor at the Imperial and Royal German University, Prague, and J. BISHOP TINGLE, PH.D., F.C.S., Professor of Chemistry at McMaster University, Toronto, Canada. Third Edition, Revised. New York: John Wiley and Sons; London: Chapman and Hall, Limited. 1908. pp. XIV + 218.

The new matter in the second edition of this excellent treatise on the qualitative and quantitative determination of radicles in carbon compounds is found in the appendix of 55 pages. Recent uses of alkylating agents, isocyanates, the Teisel method, etc., are described in detail. One of the most important features of this book is the large number of references, a feature which English texts on chemistry too often lack.

S. F. ACREE.

[1] J. Phys. Chem., **9**, 277; **12**, 36.